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Performance Test Results and Comparative Data for Designated Equilvalent Methods for Sulfur Dioxide

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Performance Test Results and Comparative Data for Designated Equivalent Methods for Sulfur Dioxide

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The U.S. Environmental Protection Agency designates specific ambient monitoring methods and analyzers as reference or equivalent methods acceptable for use in certain required monitoring. Such designation is based on test of the performance of the analyzer model by the manufacturer (or other applicant) prior to designation. After designation, EPA carries out further tests of the analyzer, including performance tests as well as comparative tests to evaluate the performance, reliability, and operational peculiarities of the analyzer with respect to other analyzers monitoring the same pollutant.

This report summarizes both the manufacturer's predesignation test results and the available EPA postdesignation test results for currently designated sulfur dioxide analyzers. Manufacturer's predesignation test results are presented for thirteen analyzers, and all test results met or exceeded the specifications. EPA postdesignation performance test results are presented for ten analyzers, and similarly, all test results met or exceeded the specifications. EPA postdesignation comparative test results are presented for eight analyzers, with the results indicating that the analyzers tested were generally stable and reliable and demonstrated a high degree of comparability.

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a. DESCRIPTORS	b. IDENTIFIERS/OPEN ENDED TERMS	c. COSATI Field/Group

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PREFACE

Measurement and monitoring research efforts are designed to anticipate potential environmental problems, to support regulatory actions by developing an in-depth understanding of the nature and processes that impact health and the ecology, to provide innovative means of monitoring compliance with regulations, and to evaluate the effectiveness of health and environmental protection efforts through the monitoring of long-term trends. The Environmental Monitoring Systems Laboratory, Research Triangle Park, NC, has responsibility for: assessing environmental monitoring technology and systems; implementing Agency-wide quality assurance programs for air pollution measurement systems; and supplying technical support to other groups in the Agency, including the Office of Air, Noise, and Radiation, the Office of Toxic Substances, and the Office of Enforcement.

Assessment of environmental monitoring technology is performed in part by the Quality Assurance Division. Through the Equivalency Testing Program, automated analyzers are evaluated to ensure that explicit performance specifications are met. This document is one in a series of four that summarizes performance test results and comparative data obtained during analyzer evaluations. The series will document evaluations of analyzers that monitor ambient air for ozone, oxides of nitrogen, sulfur dioxide, and carbon monoxide.

ABSTRACT

Under Part 53 of Title 40 of the Code of Federal Regulations (40 CFR Part 53), the U.S. Environmental Protection Agency designates specific ambient monitoring methods and analyzers as reference or equivalent methods acceptable for use in National Air Monitoring Stations (NAMS), State and Local Air Monitoring Stations (SLAMS), and Prevention of Significant Deterioration (PSD) monitoring. Such designation requires that extensive performance testing of the analyzer be carried out by the manufacturer (or other applicant) prior to designation. After designation, EPA carries out further tests of the analyzer. These EPA tests include performance tests as well as comparative tests to evaluate the performance, reliability, and operational peculiarities of the analyzer with respect to other analyzers monitoring the same pollutant.

This report summarizes both the manufacturer's predesignation test results and the available EPA postdesignation test results for currently designated sulfur dioxide analyzers. Manufacturer's predesignation test results are presented for 13 analyzers. The manufacturer's tests were conducted according to procedures presented in 40 CFR Part 53, and all test results met or exceeded the specifications contained therein. EPA Phase I postdesignation test results are presented for 10 analyzers. These tests were conducted according to an abridged version of the 40 CFR Part 53 procedures. Again, all test results met or exceeded the CFR specifications. EPA Phase II postdesignation test results are presented for eight analyzers. Although these tests were primarily comparative in nature with no formal performance specifications applicable to the data, the results indicated that the analyzers tested were stable, reliable, and demonstrated a high degree of comparability among themselves.

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ABBREVIATIONS AND SYMBOLS

ABBREVIATIONS

cm^3/min --cubic centimeter per minute
CFR --Code of Federal Regulations
DAMDF --Durham Air Monitoring Demonstration Facility
EMSL --Environmental Monitoring Systems Laboratory
EPA --U.S. Environmental Protection Agency
FPD --flame photometric detection
h --hour
Hz --hertz (frequency in cycles per second)
kPa --kilo pascal
L --liter
LDL --lower detectable limit
MDL --minimum detectable limit
mm --millimeter
MSB --Methods Standardization Branch
NAMS --National Air Monitoring Station
NBS --National Bureau of Standards
PCB --printed circuit board
PFD --pulsed fluorescent detection
PMT --photomultiplier tube
ppb --parts per billion
ppm --parts per million
PSD --prevention of significant deterioration
psig --pounds per square inch, gauge
QAD --Quality Assurance Division
SLAMS --State and Local Air Monitoring Station
SRM --standard reference material
torr --unit of pressure (1 mm Hg @ 0° C or 133 N/m^2)
TFE --tetrafluoroethylene (Teflon)
μm --micrometer
URL --upper range limit
UV --ultraviolet
Vac --volts, alternating current

SYMBOLS

~ --approximately
CO --carbon monoxide
CO_2 --carbon dioxide
H_2O --water
$H_2O(v)$ --water vapor
NO --nitric oxide
NO_x --oxides of nitrogen
NO_2 --nitrogen dioxide
O_3 --ozone
SO_2 --sulfur dioxide

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SECTION 1

INTRODUCTION

Under Part 53 of Title 40 of the Code of Federal Regulations (40 CFR Part 53), the U.S. Environmental Protection Agency (EPA) designates specific ambient monitoring methods and analyzers as acceptable for use in National Air Monitoring Stations (NAMS), State and Local Air Monitoring Stations (SLAMS), and Prevention of Significant Deterioration (PSD) monitoring, among other monitoring applications. These methods are designated as reference methods or equivalent methods, depending on whether or not the method employs a particular measurement principle and calibration procedure specified for each pollutant in 40 CFR Part 50. A list of all currently designated methods is available from the Quality Assurance Division (QAD) or from the Quality Control Coordinator at any EPA Regional Office.

Commercial analyzer models are designated as reference or equivalent methods based on an application submitted by the manufacturer (or other applicant). This application must show that a test analyzer representative of the analyzer model meets the following criteria:

1. It has been tested according to specific test procedures prescribed in 40 CFR Part 53;

2. It meets prescribed minimum performance specifications; and

3. It meets certain other requirements such as having a suitable calibration procedure and an adequate operation and instruction manual.

Any designated analyzer model should meet the requirements mentioned above. However, these analyzer models may differ considerably in design, features, reliability, measurement principle, ease of operation, and level of performance above the required minimum. These factors allow for intelligent selection of the best or most appropriate analyzer for a particular application.

The Methods Standardization Branch (MSB) of the Environmental Monitoring Systems Laboratory (EMSL) at Research Triangle Park, NC, is responsible for EPA's reference and equivalent method designation program for ambient air monitoring methods. In this capacity, MSB acquires performance data and other information on these methods, particularly on the various commercial analyzer models that have been designated as reference or equivalent methods.

To summarize this information and make it available to those who may find it beneficial in selecting analyzers, MSB, with the assistance of the Research Triangle Institute (RTI), has prepared this report on designated methods for sulfur dioxide (SO_2). Other reports discuss designated methods for ozone, nitrogen dioxide, and carbon monoxide.

The information presented in this report is derived from the following sources:

1. Predesignation test data submitted by the applicant,
2. Postdesignation tests conducted by MSB,
3. Reports or comments from analyzer users, and
4. Other pertinent information as needed.

The predesignation test data were extracted from the application for designation submitted by the applicant (usually the analyzer manufacturer) and were thus obtained from tests conducted at the applicant's own laboratory or test site. These tests must be conducted in accordance with the explicit test procedures specified in 40 CFR Part 53. Results must then be calculated and interpreted according to the prescribed specifications.

The postdesignation tests conducted by MSB are part of an ongoing postdesignation test program and may include one or more of the following types:

1. Phase I tests are laboratory performance tests similar to the predesignation tests required by 40 CFR Part 53;
2. Phase II tests simulate actual use conditions and serve to intercompare designated methods; and
3. Phase III tests are special purpose tests for specific analyzers and are used when unique needs or circumstances arise.

Postdesignation test results are the major source of information in this report and are described in detail in Section 2. The tests are conducted either by Quality Assurance Division personnel or by a contractor, under QAD direction, who has no contractual or financial association with any commercial manufacturers of designated analyzers. Because of resource limitations, there may be substantial delays in completing the postdesignation tests of an analyzer model following its designation as a reference or equivalent method.

The information in this report is based on files maintained by MSB for each designated method. MSB encourages analyzer users to submit comments that might be of interest to others using or contemplating purchase of a designated analyzer. Such comments, particularly negative comments, are more valuable if they are accompanied by supporting data, records, or other documentation. Pertinent information from other sources, such as other EPA groups, testing laboratories, and manufacturers will also be included when available. Publication of an updated report will be considered whenever significant new information is available.

Additional information on any aspect of the report may be obtained from MSB. The report is not intended to recommend or endorse any particular analyzer over others. MSB welcomes any comments on the usefulness of these reports or suggestions for improvement. Remarks may be mailed to the address on the front page or made by phone to any of the following numbers:

Commercial:	(919) 541-2622
	(919) 541-3791
FTS:	629-2622
	629-3791

SECTION 2

POSTDESIGNATION TESTING

Because the primary predesignation testing of an analyzer is carried out by the manufacturer or other applicant, it is EPA's general policy to perform followup performance tests on the analyzer after designation. These tests are referred to as postdesignation tests and are of three types: Phase I, Phase II, and Phase III. Phase I and II tests are described below. Phase III tests include any special tests or special circumstances not covered by Phase I and II and are conducted only when deemed necessary or appropriate.

The postdesignation tests are usually carried out after designation on an analyzer purchased by EPA through normal procurement procedures. Occasionally, an analyzer purchased prior to designation is returned to the manufacturer for upgrading to designated status. Commercially unavailable analyzers are borrowed for the tests. The manufacturer is always notified of the testing to be done and of the fact that the test analyzer obtained is assumed to be representative of the model. Because of the complex nature of most analyzers, variability in performance from one instrument to another can be expected. Even though all analyzers must be within the required specifications, this potential variability must be kept in mind when the test results in this report are considered and compared with those of other analyzers.

PHASE I TESTS

General Description

Phase I tests are laboratory performance tests that are conducted in accordance with the same test procedures and specifications required for the applicant's predesignation tests. The one exception is that fewer trials (usually four) are performed for each test parameter to reduce costs. All calibrations, test apparatus, pollutant standards, test procedures, test atmospheres, and test documentation are as specified in 40 CFR Part 53. An individual report containing more detailed information on the Phase I test for each analyzer tested is available from MSB.

Analyzers to be Phase I tested are set up and allowed to operate for several weeks prior to actual testing. During this startup period, preliminary calibrations and linearity checks are performed to verify proper operation. In the event that unusual behavior such as nonlinearity or inoperability due to a major malfunction is identified, the manufacturer is notified. The manufacturer is encouraged to become involved throughout the startup period so that potential problems may be identified prior to testing. If a failure occurs during testing, the manufacturer is notified and given the opportunity to repair the analyzer. At the conclusion of the test, all failures and manufacturer involvement are documented and reported.

Data Interpretation

The Phase I test results for each analyzer are shown in Tables 3 through 15 along with the EPA performance specifications and the applicants' own predesignation test data (as submitted in the equivalency application). The results reported are averages of several trials for each parameter (usually four trials for the EPA Phase I data and seven for the applicant's predesignation data). The test results must generally be less than (or within) the EPA performance specifications shown for an analyzer to achieve designation, and, except for the lower detectable limit, these results are comparable in a relative sense from one instrument to another. The manufacturer's advertised or claimed performance specifications, however, may not be directly comparable to the test data or to other analyzers since manufacturers may choose to define their performance specifications, or how they are measured, differently. The various EPA performance parameters are described briefly below along with pertinent comments. See 40 CFR Part 53 for the formal definitions of the performance parameters and the prescribed test procedure for each.

Noise--

Noise refers to short-term deviations in the analyzer output that are not caused by changes in the input concentration. Noise is measured at both 0 percent and 80 percent of the upper range limit (URL) and is the standard deviation of 25 readings taken at 2-minute intervals. Normally, this value will be slightly less than the average absolute deviation from the mean value and is usually much less than the peak-to-peak noise.

Lower Detectable Limit--

The lower detectable limit (LDL) is the smallest pollutant concentration that produces an output change of at least twice the noise level. The test does not determine the actual LDL; it only verifies that the output signal at an input concentration of 0.01 ppm is at least two times the 0-ppm noise level. Therefore, the value reported is usually close to 0.01 ppm and must be greater than twice the noise level. An output signal significantly lower than 0.01 ppm may indicate a nonapparent negative zero offset or other low-level response problems.

Interference Equivalent--

The interference equivalent is the relative degree of unwanted response caused by compounds other than sulfur dioxide present in the ambient air sample. The reported values should not be interpreted as the actual error to be expected in ambient measurements because the test concentrations of most of the interferents are higher than those normally encountered in ambient air. However, the values for water and carbon dioxide (CO_2) do represent the approximate error that may result when the calibration gases are dry and/or free of CO_2.

Zero Drift (12 h)--

The 12-h zero drift is the maximum change in continuous output response to zero input concentration over a 12-h period of unadjusted operation. The 12-h zero drift includes any peak-to-peak noise component, so it may be higher than the 24-h zero drift.

Zero Drift (24 h)--

The 24-h zero drift is the net change in response to zero input concentration between two points in time ~24 h apart during unadjusted analyzer operation. It includes zero drift caused by changes in ambient temperature, line voltage, or both. The 24-h zero drift tends to be sometimes positive, sometimes negative; hence the average would be misleadingly low. Therefore, the average of the absolute values of the analyzer's daily drift is reported in Tables 3 through 15 as a more meaningful value.

Span Drift (20% URL)--

The span drift at 20 percent URL is the net change in response to an input concentration of ~20 percent of the URL between two points in time ~24 h apart during unadjusted analyzer operation and including the effects of changes in ambient temperature, line voltage, or both. Because the test procedure specifies no correction for zero drift, the reported value represents a combination of both zero drift and span drift over the period. The average of the absolute values is reported.

Span Drift (80% URL)--

The span drift at 80 percent URL is the net change in response to an input concentration of ~80 percent of URL between two points in time ~24 h apart during unadjusted analyzer operation and including the effects of changes in ambient temperature, line voltage, or both. The 80-percent URL span drift is also calculated without a correction for zero drift; therefore it may be higher or lower than the actual change in the slope of the calibration curve. Again, the average of the absolute values of the individual daily results is reported.

Lag Time--

Lag time is the time required to observe the first change in response resulting from a sudden change in input concentration.

Rise Time--

Rise time is the time (not including the lag time) required for the response to reach 95 percent of its final value after a sudden increase in the input concentration.

Fall Time--

Fall time is the time (not including lag time) required for the response to decrease to 5 percent of its previous value when the input concentration is suddenly changed to 0 ppm.

Long lag, rise, or fall times generally do not adversely affect measurements expressed as hourly averages and may even be beneficial where concentrations fluctuate rapidly. However, long response times may be an annoyance or source of error during calibration and zero and span drift adjustment.

Precision--

Precision is the variation in the response value to six repeated measurements of the same upscale pollutant concentration, approached alternately from lower and higher concentrations. The reported precision is a measure of the repeatability of the analyzer and is determined at both 20 and 80 percent of the URL.

PHASE II TESTS

General Description

Phase II tests are intended to test analyzers in a more or less typical ambient monitoring configuration where their stability, reliability, general performance, and operational peculiarities can be observed, recorded, and compared. The tests are conducted simultaneously on a group of analyzers during a period of several months. All analyzers measure the same pollutant in the ambient air, which is sampled from a common manifold. The ambient pollutant concentrations are sometimes augmented in the manifold with artificially generated pollutant to increase the concentration readings.

Unless otherwise specified, the Phase II tests are carried out at EPA's Durham Air Monitoring Demonstration Facility (DAMDF) in an urban/industrial/commercial area of Durham, NC. Ambient air samples for the analyzers are drawn from an intake on the building roof and distributed by an all-glass, power-ventilated manifold system. Pollutant levels are augmented, when appropriate. During such augmentation, however, all sample air contains at least 90 percent unaltered ambient air. The analyzers' inlets are connected to the manifold via Teflon® particulate filters and either 3-mm (1/8-in) or 6-mm (1/4-in) Teflon® tubing, depending on the analyzer flow rate. The sample lines are kept as short as practical.

All test analyzers are installed, calibrated, operated, and maintained in accordance with the manufacturer's operation/instruction manual and good monitoring practice. Analyzers receive a multipoint calibration initially and once per month during the test period. Two-point zero and span checks are made two or three times per week, with zero adjustments only if the zero response is not within ±3 percent of full-scale response from nominal, and span adjustments only if the span (slope of calibration curve) changes by more than ±7 percent from nominal.

Zero air is obtained from filtered ambient air by appropriate drying and chemical scrubbing. Calibration and span gases are obtained by techniques such as dilution of high concentration cylinder gases, permeation devices, and gas phase titration. Ozone (O_3) concentrations are generated by ultraviolet (UV) radiation and are traceable to a UV standard; all other pollutant concentrations are traceable to National Bureau of Standards Standard Reference Materials (NBS-SRMs).

Analyzer readings are recorded at 1-min intervals using a Monitor Labs 9300 data acquisition system. One-hour averages (50-min minimum) are automatically calculated and transferred to magnetic tape. Zero and span responses are also recorded on the tape. The tapes are read into a Hewlett-Packard 9845A Desk Top computer for verification, editing, corrections as necessary, and calculation of the various statistical comparisons.

Data Interpretation

Phase II testing is primarily intended to be comparative in nature. As such, the test does not require conformance to any formal performance specifications, and the analyzers neither "officially pass" nor "officially fail" the comparisons. The Phase II test results and other data are presented in Section 3 as a series of figures for each analyzer. The figures in each analyzer's series (Figures 4 through 8, for example) are discussed in their order of appearance. The first (Figure 4, for example) is a typical multipoint calibration curve for the analyzer, showing five or more points spaced over the full-scale range, calculated by least squares regression from the actual calibration response data. The span is normally adjusted to a slope of ~200 (scale percent/ppm) for a 0-to-0.5-ppm range. The correlation coefficient provides an empirical measure of the linear association between the analyzer response and the calibration concentrations.

The chronological records of the zero and span drift for each analyzer are shown next in the series of figures (Figure 5, for example). Zero drift is plotted in absolute units (ppm) and the span drift is plotted as the percent difference of the span slope from the nominal slope (not percent-of-scale change in an arbitrary span concentration). Both zero and span drifts are total accumulated drifts except where manual adjustments are explicitly indicated by diamonds situated on the x-axis. The drifts are referenced to the nominal intercept (0 percent of scale) and nominal slope (200) represented by the horizontal, dashed lines. Also shown are the nominal adjustment limits for zero (±3 percent of full scale or ±15 ppb) and span (±7 percent). All adjustments, whether made because nominal drift limits were exceeded or during routine calibrations, are indicated by the diamonds. It is often not possible to adjust the zero and span to the exact nominal values desired because of the nature of the controls. The drift plots are intended mainly for visual comparison among the various analyzers.

The statistics shown above each chart give (1) the total net drift over the entire test period, ignoring adjustments and resets; (2) the number of individual drift periods--i.e., periods between zero and span checks; (3) the average length of the drift periods in days; (4) the average absolute value of the drift for each period (i.e., ignoring the signs of the drifts); and (5) the standard deviation of the individual drifts over all drift periods. The marker at the right side of each chart illustrates a drift range of ±3 standard deviations.

The next figure (Figure 6, for example) is a scatter diagram comparing each subject analyzer measurement (corrected for zero and span drift) with the average of the corresponding measurements from the other analyzers during simultaneous, continuous monitoring of ambient air over approximately 150 days. The linear regression relationship estimated from the data (solid line) is shown along with a dashed line representing the ideal linear relationship (slope = 1, intercept = 0). The linear regression slope and intercept have been tested statistically to determine if they are significantly different from 1 and 0, respectively. In general, the regression slopes and intercepts are significant even though they approximate the ideal values because of the large number of points (N) used in the regression. Also shown is the sample correlation coefficient (r).

The additional dashed lines on the scatter diagram show statistical bounds that should include 90 percent of future analyzer measurements (Y) for any concentration (X) as measured by the average of the reference analyzers. This is a 95-percent confidence interval, based on the estimated linear regression and centered on the estimated regression line, applicable to 90 percent of future observations.*

During the SO_2 Phase II test, ambient levels of SO_2 were augmented ("spiked") with additional, extraneous SO_2 from a permeation system to allow evaluation of the instruments at concentration levels greater than the rather low ambient levels available at the test site. Concentration levels for the augmentation were approximately 75 ppb (15 percent of full scale), 125 ppb (25 percent of scale), and 250 ppb (50 percent of scale). Each augmentation period lasted from 15 to 19 days. These augmentation periods account for the grouping or clustering of the data points observed on the scatter diagrams.

The next figure (Figure 7, for example) presents another comparison of the differences in hourly ambient air readings between subject analyzer and the average of simultaneous readings from other analyzers. Corrections for zero and span drifts are made before the data are compared. The comparison is shown in the form of a frequency distribution indicating numerically and graphically the frequency (number of hours out of the total test period) of the occurrence of each discrepancy versus its magnitude and sign. Also given are the correlation coefficient, the mean difference (bias), the standard deviation of the differences (spread), and the number of absolute differences >20 ppb; all of these statistics are calculated with respect to the differences between the hourly readings of the subject analyzer and the average of the corresponding hourly readings from the other analyzers in the test group.

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*A more detailed description of this type of confidence interval can be found in Lieberman, G. J., and R. G. Miller, Simultaneous tolerance intervals in regression, Biometrika, 50:155-168, 1963.

Last is a figure (Figure 8, for example) showing the same type of frequency distribution discussed above but without periodic zero and span corrections; all hourly averages for the subject analyzers are based on the original calibration curve. The reference data from the analyzers on which the comparison is based are still corrected for zero and span drift. Comparison of the data in corresponding sets of frequency distributions, particularly the mean difference and the standard deviation of the differences, illustrates the effect of making periodic zero and span corrections to ambient monitoring data. Usually, the agreement of the hourly readings (bias, spread, or both) is improved by the periodic zero and span adjustments, and the practice is generally recommended where possible.

SECTION 3

TEST RESULTS AND DATA FOR DESIGNATED SULFUR DIOXIDE ANALYZERS

This section contains summary information on Phase I and Phase II postdesignation tests performed on 12 models of sulfur dioxide analyzers (see Table 1) and predesignation test data for 13 models as reported in the corresponding applications for designation as equivalent methods.

TEST RESULTS

Tables 3 through 15 summarize the available Phase I laboratory performance test results for each analyzer and compare these data with EPA specifications and with the manufacturer's predesignation test results. Phase II test results for each tested analyzer are shown in a series of figures contained in each analyzer subsection. See Section 2 for an explanation of the tests and figures.

TABLE 1. ANALYZERS INCLUDED IN THE POSTDESIGNATION TESTING OF SULFUR DIOXIDE ANALYZERS

Manufacturer	Model	Serial No.	Phase I tests	Phase II tests
ASARCO	500	None	5/78-1/79	Not anticipated
Beckman #1 Beckman #2	953 953	1000039 1000865	5/82-4/83	11/78-6/79
Bendix	8303	11252	Planned	2/79-6/79
Lear Siegler	SM1000	7564	9/76-5/77	11/78-6/79
Lear Siegler	AM2020	0910020	Planned	Not planned
Meloy	SA185-2A	4H024	10/76-11/76	11/78-6/79
Meloy	SA285E	7E140	Planned	11/78-6/79
Meloy	SA700	OF106	5/82-3/83	Not planned
Monitor Labs	8450	147	3/77-8/77	11/78-6/79
Monitor Labs #1 Monitor Labs #2	8850 8850	90 717	8/82-6/83	Not planned
Philips	PW9700	D1415C	5/78-1/79	Not planned
Philips	PW9755	612	5/78-1/79	11/78-6/79
Thermo Electron	43	ASM-3294-64	10/76-1/78	11/78-6/79

Determination of Minimum Detection Limit (MDL)

Of particular interest for any air monitoring analyzer is its minimum measurement capability. MDL can be defined as the lowest concentration that an analyzer can reliably distinguish from zero concentration. Note that this MDL is very similar to the lower detectable limit defined in 40 CFR Part 53 and discussed in Section 2. However, the test for LDL does not actually measure the LDL, it only determines that the LDL is greater than twice the noise level. In this study, an estimate of the MDL for each analyzer was determined by the following equation:

$$\text{MDL} = 3 \times \text{precision},$$

where the value 3 is the minimum recommended by the "Guidelines for Data Acquisition and Data Quality Evaluation in Environmental Chemistry"* and implies a risk of about 7 percent for concluding that a detectable concentration of SO_2 is present when the concentration is actually zero.

Rather than use the precision defined in 40 CFR Part 53 and measured in laboratory tests (Section 2) to estimate MDL, a more appropriate "total operating precision" of an analyzer was obtained from the Phase II test data. The total operating precision consists of the variance of two unpredictable, random sources of measurement error--the method precision and random bias. Random bias is caused by interfering substances that influence the ability of an analyzer to measure SO_2. The total operating precision is the square root of the sum of these two variance components.

The estimation of these components is relatively straightforward when there is a defined reference method measuring the "true" concentration or when replicate measurements are obtained. If neither reference method nor replicate measurements are available, total operating precision can be estimated by using principal component estimates as described by Lawton et al.† Using this procedure, estimates of total operating precision and corresponding estimates of MDL for five of the analyzers tested were made and are shown in Table 2.

It should be noted that these estimates of precision and MDL do not include errors associated with other operators and laboratories. Thus, these estimates are probably lower than would be determined if other variables were included.

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*Analytical Chemistry, 52:2242, December 1980.

†Lawton, W. H., E. A. Sylvestre, and B. J. Young-Ferraro, Statistical comparison of multiple analytic procedures: Application of clinical chemistry, Technometrics, 21:397-409, 1979.

TABLE 2. ESTIMATES OF TOTAL OPERATING PRECISION AND MINIMUM DETECTION LIMITS

Analyzer	Total operating precision (ppm)	Minimum detection limit (ppm)
Beckman 953	.0075	.0225
Meloy SA185-2A	.0032	.0096
Meloy SA285E	.0016	.0048
Monitor Labs 8450	.0040	.0120
Thermo Electron 43	.0059	.0177

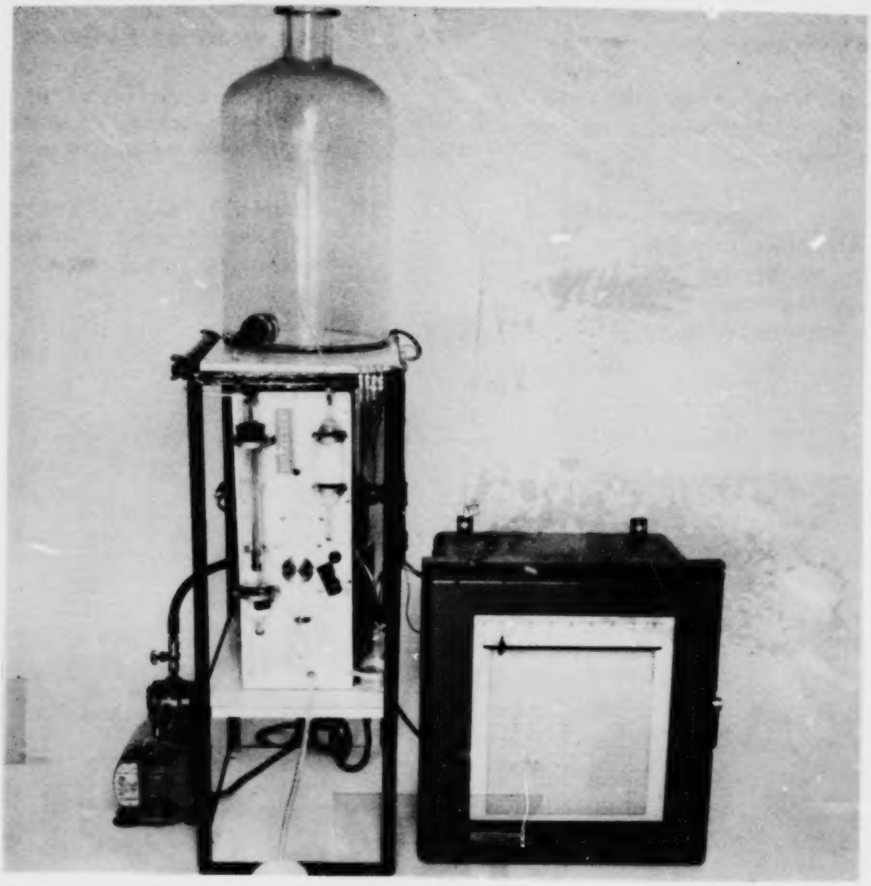


Figure 1. ASARCO Model 500 SO_2 Analyzer (EQSA-0877-024).
ASARCO Incorporated, 3422 South 700 West,
Salt Lake City, Utah 84119.

General Description

The ASARCO Model 500 SO_2 analyzer operates on the principle of conductometric detection as described in Appendix A. It is a refined version of the original SO_2 monitor developed by Dr. Moyer D. Thomas in 1928. It is equipped with an unheated chemical scrubber that removes all ambient compounds other than SO_2 that may cause conductivity changes in the absorbing solution. Such compounds include carbon dioxide, nitrogen dioxide, ammonia, and hydrogen chloride. Removal of these compounds makes the instrument specific for SO_2.

This analyzer, used only by ASARCO for monitoring at its own facilities, is not in commercial production. For that reason, Phase II testing is not planned for this analyzer.

TABLE 3. ASARCO 500 LABORATORY PERFORMANCE TEST RESULTS

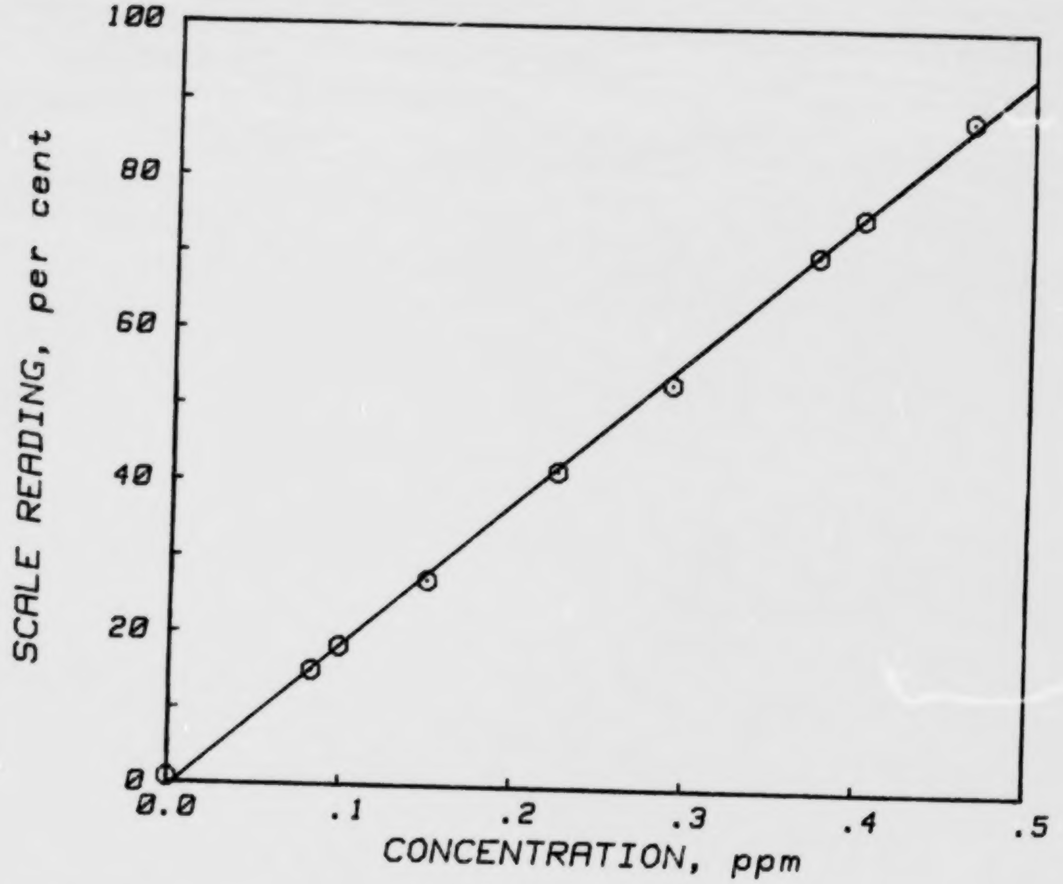
Performance parameters	Units	EPA specs.[a]	Manufacturer's test results[b]	EPA test results[c]
Noise – 0% URL	ppm	0.005	< 0.001	Not tested
Noise – 80% URL	ppm	0.005	0.002	Not tested
Lower detectable limit	ppm	0.01	0.006	0.008
Interferents	ppm			
CO_2		±0.02	0.002	0.011
NO_2		±0.02	0.002	0.011
NH_3		±0.02	0.001	0.000
HCl		±0.02	0.001	0.008
Total		< 0.06	0.006[d]	0.030[d]
Zero drift – 12 h	ppm	±0.02	0.001[d]	0.001[d]
Zero drift – 24 h	ppm	±0.02	0.001[d]	0.001[d]
Span drift – 20% URL	%	±20.0	0.78[d]	2.6[d]
Span drift – 80% URL	%	±5.0	1.42[d]	2.8[d]
Lag time	min	20	0.5	Not tested
Rise time	min	15	0.5	Not tested
Fall time	min	15	0.5	Not tested
Precision – 20% URL	ppm	0.010	0.001	0.005
Precision – 80% URL	ppm	0.015	0.006	0.012

[a] From EPA equivalency regulations, 40 CFR Part 53.

[b] Average, from manufacturer's application for equivalency determination.

[c] Average, from EPA Phase I postdesignation tests.

[d] Average absolute values.



ANALYZER: ASARCO
MODEL: 500
SERIAL No.: NONE
POLLUTANT: SO2
RANGE: .5 ppm
LOCATION: RTI
DATE: 05/22/78
DATE CODE: 78.142
NAME: PHASE I

$Y = MX + A$

M = 188.847
95% C.I.= ± 4.566

A = −.529
95% C.I.= ± 1.265

r = .99963

DATA:	X	Y
1	0.000	.750
2	.083	15.000
3	.099	18.200
4	.150	27.000
5	.225	41.600
6	.291	53.200
7	.375	70.200
8	.401	75.300
9	.464	88.300

Figure 2. Typical calibration curve for the ASARCO Model 500.

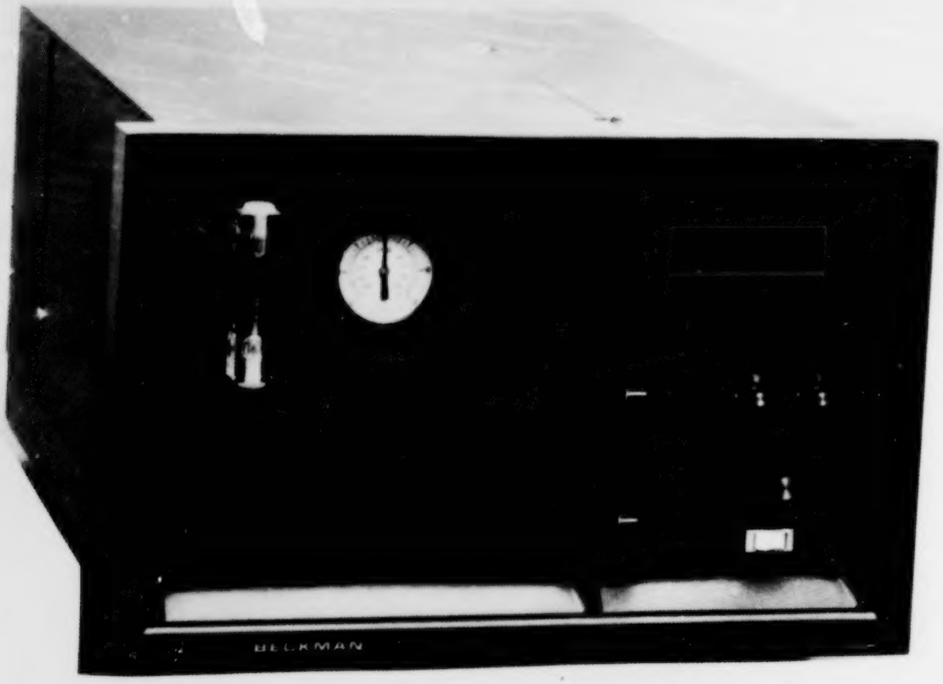


Figure 3. Beckman Model 953 Fluorescent Ambient SO_2 Analyzer (EQSA-0678-029). Beckman Instruments, Inc., Process Instruments Division, 2500 Harbor Drive, Fullerton, CA 92634.

General Description

The Beckman Model 953 sulfur dioxide analyzer operates on the principle of fluorescence as described in Appendix A. It uses mechanically chopped ultraviolet radiation to provide signal modulation for amplification. The instrument is equipped with a heated "reactor" (scrubber) to remove aromatic hydrocarbons that would otherwise produce a positive interference in the fluorescence technique. The heated reactor, however, will convert ambient hydrogen sulfide (which does not interfere with the fluorescence technique) into sulfur dioxide, causing an interference. To prevent this interference, an unheated chemical scrubber for hydrogen sulfide is placed upstream of the hydrocarbon reactor. Removal of moisture from the sample is not required in this analyzer because this potential interference is minimized by judicious selection of the wavelength of the excitation radiation.

To be used as an equivalent analyzer, the Model 953 must be operated on the 0-to-0.5-ppm or 0-to-1.0-ppm range, with a time constant setting of 2.0, 2.5, or 3.0 minutes and with a 5-to-10-μm membrane filter element installed in the rear panel filter assembly. The analyzer can be operated with or without any of the following options:

- Remote operation kit (Catalog No. 641984)
- Digital panel meter (Catalog No. 641710)
- Rack mount kit (Catalog No. 641709)
- Panel mount kit (Catalog No. 641708).

Ambient air surrounding the analyzer must be within the range of 20° to 30° C, inclusive, and line voltage to the analyzer must be within the range of 105 to 125 Vac, inclusive.

TABLE 4. BECKMAN 953 LABORATORY PERFORMANCE TEST RESULTS

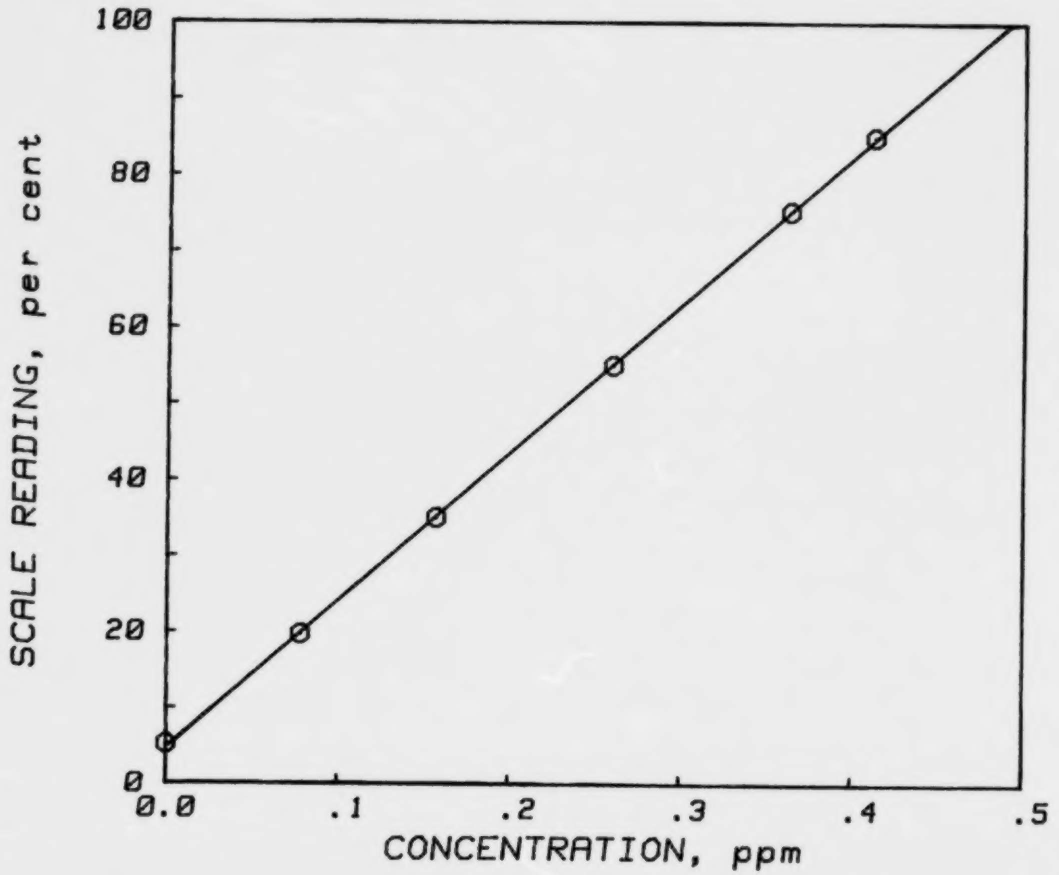
Performance parameters	Units	EPA specs.[a]	Manufacturer's test results[b]	EPA test results[c]
Noise — 0% URL	ppm	0.005	0.001	0.001
Noise — 80% URL	ppm	0.005	0.002	0.002
Lower detectable limits	ppm	0.01	0.010	0.009
Interferents	ppm			
H_2S		±0.02	0.001	0.001
Meta-xylene		±0.02	0.002	0.007
Naphthalene		±0.02	0.001	0.005
H_2O		±0.02	0.006	−0.010
NO		±0.02	0.005	<0.001
NO_2		±0.02	0.004	−0.002
O_3		±0.02	0.004	−0.014
Total		≤0.06	0.023[d]	0.040[d]
Zero drift — 12 h	ppm	±0.02	0.003[d]	0.003[d]
Zero drift — 24 h	ppm	±0.02	0.001[d]	0.001[d]
Span drift — 20% URL	%	±20.0	1.05[d]	3.23[d]
Span drift — 80% URL	%	±5.0	0.58[d]	1.62[d]
Lag time	min	20	0.3	0.2
Rise time	min	15	6.2	2.3
Fall time	min	15	5.1	2.3
Precision — 20% URL	ppm	0.010	0.001	<0.001
Precision — 80% URL	ppm	0.015	0.002	0.001

[a] From EPA equivalency regulations, 40 CFR Part 53.

[b] Average, from manufacturer's application for equivalency determination.

[c] Average, from EPA Phase I postdesignation tests.

[d] Average of absolute values.



ANALYZER: BECKMAN
MODEL: 953
SERIAL No.: 1000039
POLLUTANT: SO2
RANGE: .5 ppm
LOCATION: DAMDF
DATE: 03/30/79
DATE CODE: 79.089
NAME: PHASE II

Y = MX + A

M = 194.000
95% C.I.= ± 2.459

A = 4.787
95% C.I.= ± .635

r = .99996

DATA:	X	Y
1	0.000	5.200
2	.078	19.700
3	.157	35.000
4	.260	55.000
5	.363	75.200
6	.412	85.000

Figure 4. Typical calibration curve for the Beckman 953.

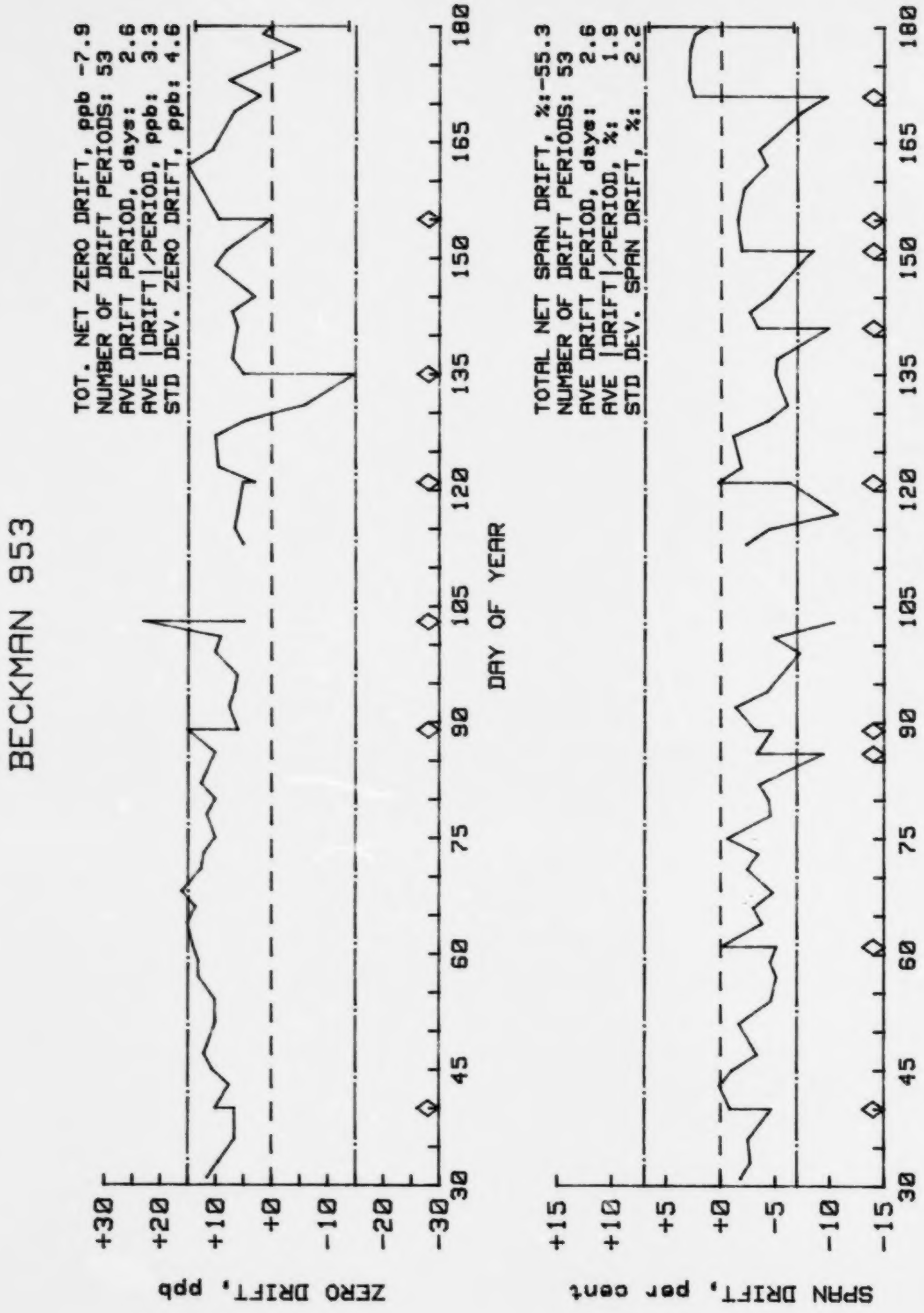


Figure 5. Zero and span drift in the Beckman 953 SO_2 readings during the Phase II ambient monitoring test.

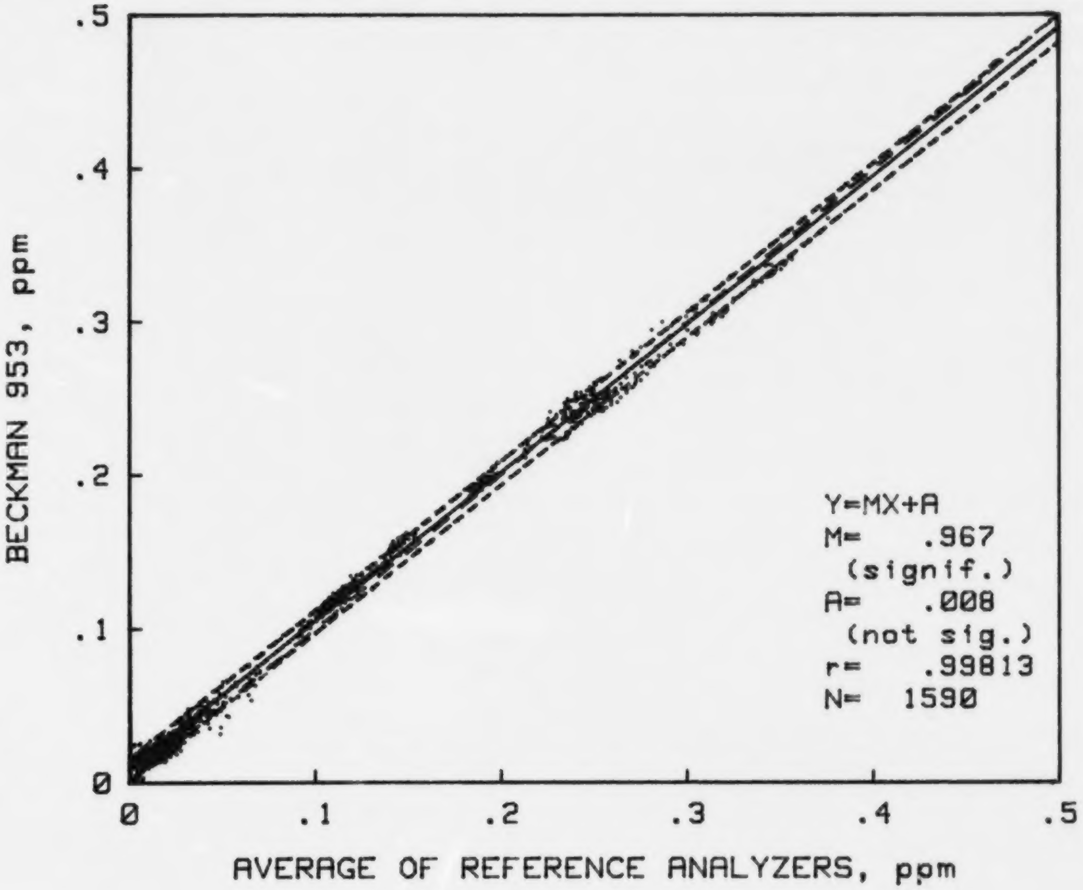
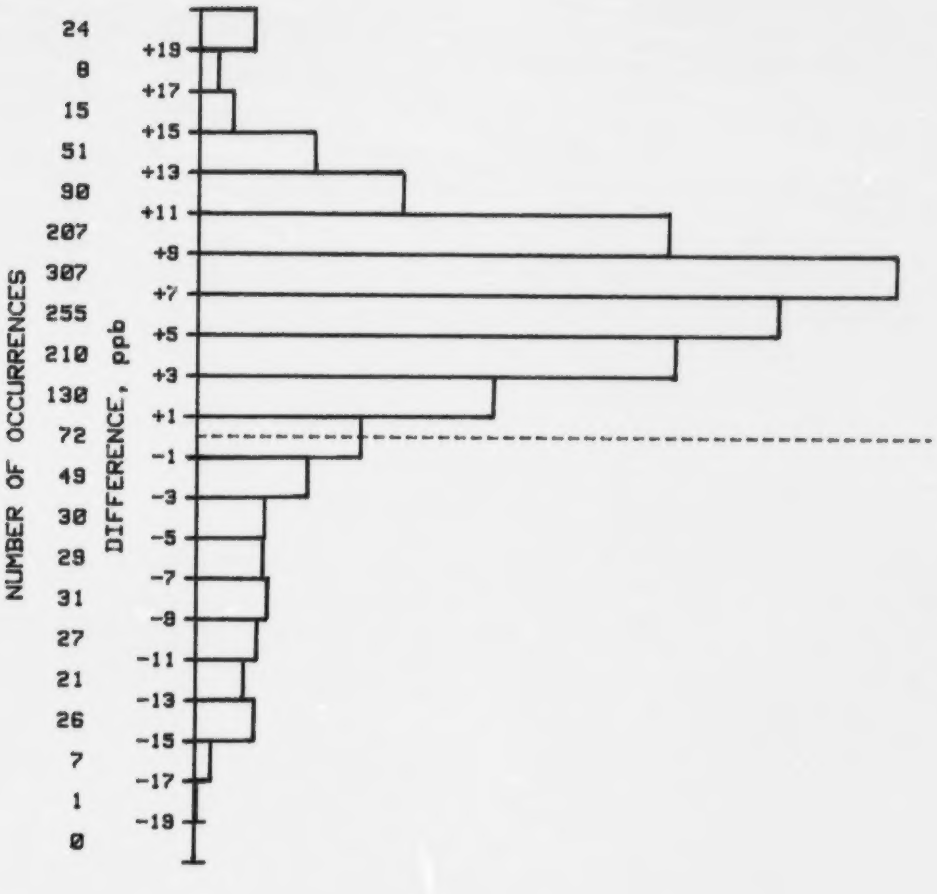
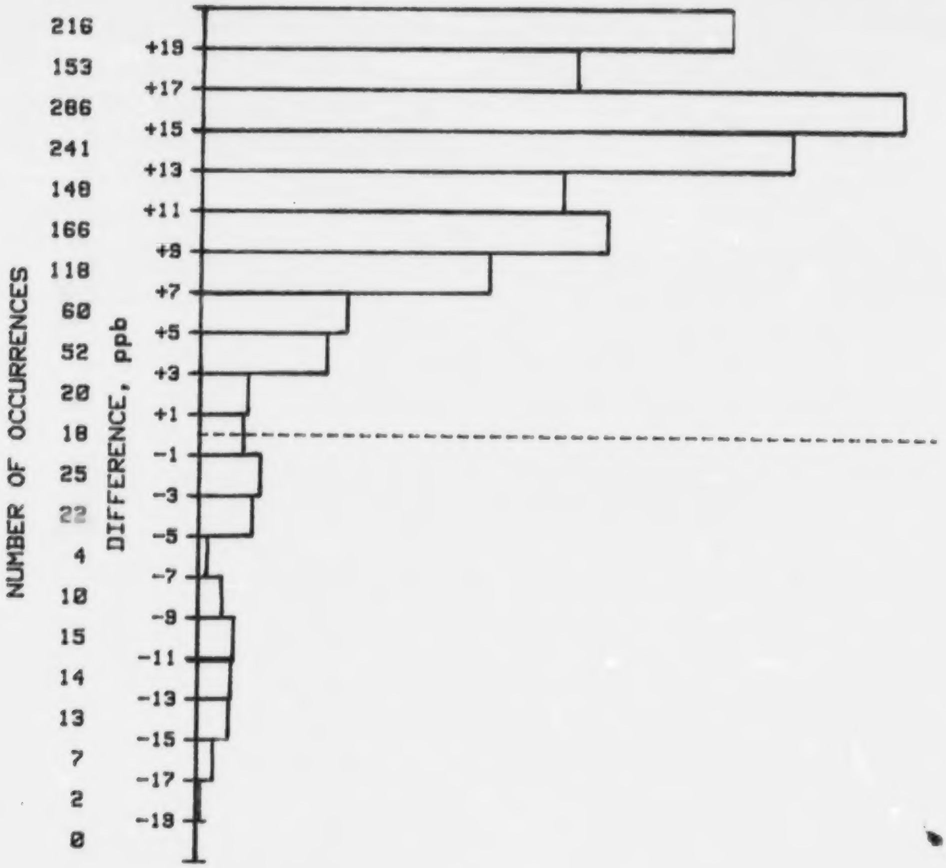


Figure 6. Relationship between the Beckman 953 and the average of the other analyzers during the Phase II ambient monitoring test (before HC reactor replacement--see General Comments).



```
TOTAL No. OF DATA PAIRS:                 1590
CORRELATION COEFFICIENT:                    .998131
MEAN DIFFERENCE, ppb:                      +5.16
STD. DEVIATION OF DIFFERENCES, ppb:   6.5720
MAX. ABSOLUTE DIFFERENCE, ppb:             25
NO. ABSOLUTE DIFFERENCES >20:              21
```

Figure 7. Frequency distribution of differences in hourly SO_2 ambient air readings between the Beckman 953 and the average of simultaneous readings from the other analyzers during the Phase II ambient monitoring test (before HC reactor replacement--see General Comments). All readings corrected for zero and span drift.



```
TOTAL No. OF DATA PAIRS:                1590
CORRELATION COEFFICIENT:                  .998363
MEAN DIFFERENCE, ppb:                   +12.39
STD. DEVIATION OF DIFFERENCES, ppb:       7.8484
MAX. ABSOLUTE DIFFERENCE, ppb:           33
NO. ABSOLUTE DIFFERENCES >20:           178
```

Figure 8. Frequency distribution of differences in hourly SO_2 ambient air readings between the Beckman 953 and the average of simultaneous readings from the other analyzers during the Phase II ambient monitoring test (before HC reactor replacement--see General Comments). Beckman 953 readings are not corrected for zero and span drift.

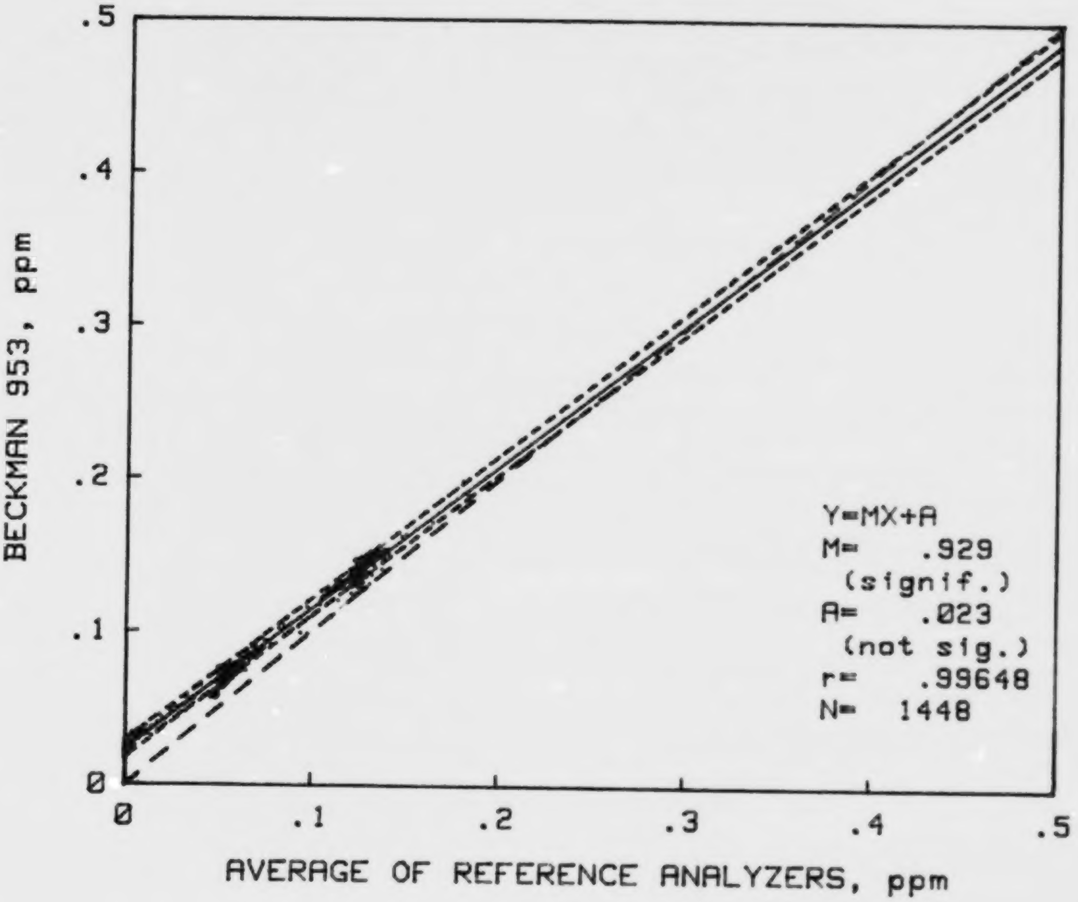
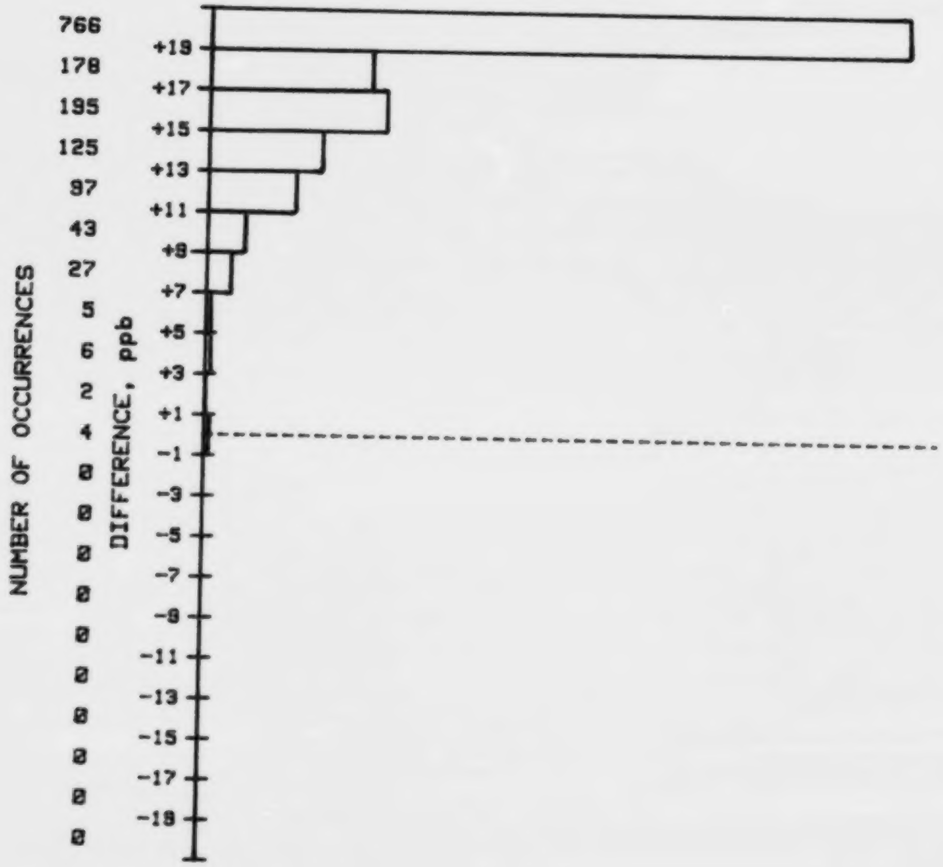
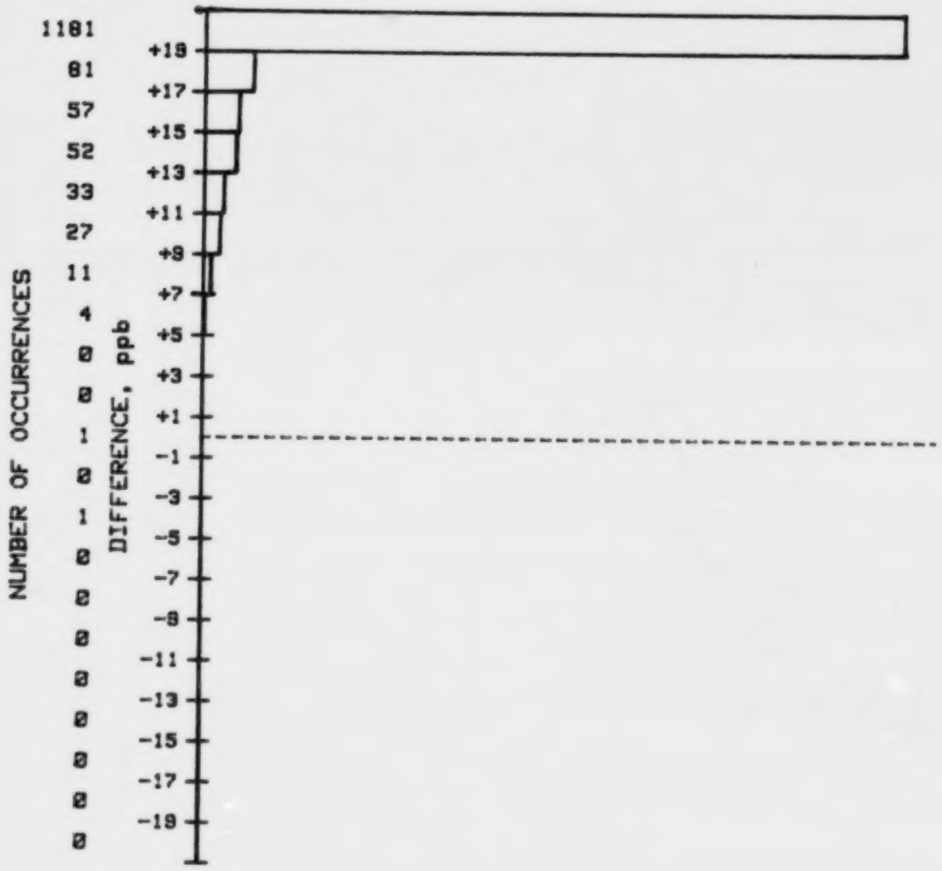


Figure 9. Relationship between the Beckman 953 and the average of the other analyzers during the Phase II ambient monitoring test (after HC reactor replacement--see General Comments).



```
TOTAL No. OF DATA PAIRS:                 1448
CORRELATION COEFFICIENT:                      .996479
MEAN DIFFERENCE, ppb:                     +19.50
STD. DEVIATION OF DIFFERENCES, ppb:        5.5777
MAX. ABSOLUTE DIFFERENCE, ppb:            30
NO. ABSOLUTE DIFFERENCES >20:            668
```

Figure 10. Frequency distribution of differences in hourly SO_2 ambient air readings between the Beckman 953 and the average of simultaneous readings from the other analyzers during the Phase II ambient monitoring test (after HC reactor replacement--see General Comments). All readings corrected for zero and span drift.



```
TOTAL No. OF DATA PAIRS:                  1448
CORRELATION COEFFICIENT:                      .993255
MEAN DIFFERENCE, ppb:                      +24.13
STD. DEVIATION OF DIFFERENCES, ppb:    6.5539
MAX. ABSOLUTE DIFFERENCE, ppb:           39
NO. ABSOLUTE DIFFERENCES >20:          1097
```

Figure 11. Frequency distribution of differences in hourly SO_2 ambient air readings between the Beckman 953 and the average of simultaneous readings from the other analyzers during the Phase II ambient monitoring test (after HC reactor replacement--see General Comments). Beckman 953 readings are not corrected for zero and span drift.

Manufacturer's Recommended Maintenance

Operation	Frequency
Replace sample filter.	Every 30 days
Check span gas solenoid valve.	Every 30 days
Refill or replace interferent reactor.	Every 90 days
Replace selective scrubber cartridge.	Every 24 mo
Replace activated carbon scrubber.	Every 24 mo
Check and/or service pump.	Every 24 mo
Check or replace source lamp.	Every 10,000 h (~417 days of continuous operation)

Malfunctions

5-14-82	During Phase I postdesignation setup and calibration (see General Comments for analyzer history), the analyzer's fuse blew due to failure of the reaction chamber heater. Replacement of the heater corrected the problem.
8-5-82	Phase I ozone interferent test failure (see General Comments).
8-20-82	After being shut down for 2 weeks, the analyzer would not respond to sulfur dioxide. The malfunction was caused by failure of the demodulator board.
10-21-82	Phase I span drift test failure on day 3 of the test procedure (see General Comments).
12-21-82	Phase I hydrogen sulfide interferent test failure. The malfunction was corrected by replacing the H_2S scrubber with a new scrubber (see General Comments) and repeating the H_2S interferent test procedure.
3-29-83[a]	Phase I span drift test failure on day 1 of the test procedure. Cause for malfunction not determined (see General Comments).
4-14-83[b]	Phase I span drift test failure on day 3 of the test procedure. The malfunction was caused by failure of the interferent reactor temperature control circuit (see General Comments).

---

[a] Modified 953, SN 1000039.

[b] New 953, SN 1000865.

General Comments

The Beckman 953 SO_2 analyzer was purchased in October 1978 and immediately included in the postdesignation Phase II testing program conducted from November 27, 1978, to June 29, 1979.

The preventive maintenance section of the instrument manual for the Beckman 953 states that the hydrocarbon reactor should be replaced routinely every 3 months. In April 1979, during Phase II testing, the reactor was replaced during routine, preventive maintenance. The sample inlet filter was also replaced during the maintenance operation.

In addition to routine preventive maintenance, corrective maintenance was performed, which included replacement and alignment of the lamp and adjustment of the photomultiplier tube (PMT) high voltage. This corrective maintenance was suggested by Beckman personnel to gain additional range for the span adjustment. The span setting had gradually increased from a pot setting of 861 to 999 (fully clockwise) during the course of Phase II testing. This fully clockwise setting was not sufficient to bring the span response within ±7 percent of the nominal span value. To correct this situation, the lamp was replaced and the PMT high voltage was adjusted from -1080 volts to -1119 volts. After adjustment, the span pot setting necessary to accomplish a nominal span response was 625.

A significant change in the instrument's response to ambient air samples was noted after this maintenance. Before maintenance, the mean difference and the standard deviation of the differences between the 953 responses and the average of the other analyzer responses had been +4.4 ppb and 7.5 ppb, respectively (see Figures 6 through 8). After maintenance, the mean difference jumped to +20.1 ppb, while the standard deviation remained essentially unchanged at 7.1 ppb (see Figures 9 through 11). However, responses to zero and span gases remained normal before and after maintenance. These observations indicated that change in performance on ambient air samples could not be attributed to the corrective maintenance operations because these operations affect zero/span analyses and ambient analyses equally. The performance change must therefore have resulted from a change in the interaction between some compound in the ambient air sample and the new reactor material. This change in interaction apparently produced a positive response.

Because the change in performance was apparently caused by a positive interference rather than an increased sensitivity for SO_2, Phase-I-type interference tests were conducted for two likely interferents: hydrogen sulfide and naphthalene. The resulting interference equivalents were +0.003 ppm for H_2S and +0.001 ppm for naphthalene. Evidently, neither of these compounds could have caused the problem.

At present, neither the cause of the suspected interference nor the actual reason for the performance difference between the "old" and "new" reactor is known. Additional testing to characterize this phenomenon is planned during Phase I postdesignation testing of the instrument.

The Phase II test program was completed on 6-29-79. At this time the analyzer was removed from service.

In April 1980, prior to the initiation of Phase I testing, the analyzer was sent to Beckman at Fullerton, California, for modification to current production configuration. It was returned to EPA in May 1980.

On June 16, 1980, upon initial startup, the analyzer did not respond to SO_2. When the problem could not be resolved by the installation of new high-voltage supply and amplifier boards (supplied by Beckman), a Beckman service representative replaced the demodulator board (the board was loose and the chopper blade was hitting the photosensor), adjusted the chopper blade for proper clearance, checked the system for leaks, replaced the amplifier board, and aligned the UV lamp. The analyzer remained operational until September 25, 1980, when it again did not respond to SO_2. Troubleshooting indicated a bad amplifier board. The analyzer was removed from the test program.

After consultations with Beckman personnel concerning the poor operational history of this analyzer, the unit was returned to the factory in the spring of 1982 for refurbishment under warranty. Corrective actions performed during the refurbishment included replacing the pump and pump shock mounts, the PNA converter, the H_2S and zero air scrubbers, the PMT, the PMT housing O-ring, a socket assembly, strip marker-14, and the source lamp. Replacements to update the analyzer to current manufacturing status were also made during the refurbishment. They included addition of a holder; replacement of the H_2 lamp supply, high-voltage, filament control, and interconnect boards; and replacement of the reaction chamber.

The analyzer was returned to EPA in April 1982. Beckman indicated that, "Subsequent to the installation of these components, the analyzer was tested in accordance with the PID test procedure 641968 for the Model 953. The analyzer's performance was equal to or better than the specifications required in the test procedure." Although originally purchased in October 1978, the analyzer, with the above stated refurbishment, could be considered a new analyzer as of April 1982.

On August 5, 1982, the analyzer failed the ozone interferent test. Additional ozone interferent tests conducted by Beckman on a current production analyzer did not result in test failures but indicated somewhat larger (but still within EPA specifications) ozone interference values than those of the original test analyzer used for the original equivalency application tests. The discrepancy was attributed to different PNA converter operational temperatures. The temperature variance appears to be attributable to a Beckman-instituted change in the supplier of the PNA converter heating blanket used in the analyzer.

On October 21, 1982, the analyzer failed a span drift test. Again Beckman was contacted. Additional span drift tests conducted by Beckman on a current production analyzer confirmed the span drift test failure. This performance deficiency was attributed to inadequate reaction chamber and air bath temperature control at high temperatures ($\geq 30°$ C) and was corrected by modifying the analyzer back cover panel to allow the entrance of additional ambient air to the analyzer.

On December 21, 1982, the analyzer failed the hydrogen sulfide interferent test. This performance deficiency was corrected by installing a new selective scrubber. The cause of the selective scrubber failure has not been determined.

On March 29, 1983, the modified analyzer (slotted back cover panel) failed a span drift test. A Beckman service representative arrived the week of April 4th to try to determine the cause of the malfunction and, if possible, to repair the analyzer. After 3 days of unsuccessful attempts to determine the cause of the malfunction, a new 953 analyzer (SN 1000865) was sent from Beckman.

On April 14, 1983, the new 953 analyzer, with a modified back cover panel, failed a span drift test. On April 20, 1983, a Beckman service representative attributed the malfunction to a failure of the interferent reactor temperature control circuit. Subsequent to replacement of the interferent reactor temperature control board, the new 953 analyzer successfully passed a repeated span drift test.

Phase II Testing Operator's Comments

This analyzer required 20 to 40 minutes to achieve equilibrium on span gases, a significant inconvenience during calibration.

During 150 days of Phase II testing, data were lost for 12 days due to malfunctions.

The compartmentalized design of this analyzer was a convenient feature during maintenance procedures.

Omission of Data from the Beckman 953 in Computation of Averages Used for Phase II Comparisons

In the frequency distributions developed from Phase II test data, each analyzer is compared to the average response from the other analyzers. Ideally, this average is assumed to represent the "real" or theoretical concentration of the sample. Nonrandom deviations (e.g., malfunctions or consistent bias) in any analyzer included in this averaging process would degrade the quality of the average and, thus, the entire comparison. Although it is not possible to eliminate nonrandom deviations completely, it is possible to eliminate or at least minimize obvious ones.

A significant change in this analyzer's performance during the Phase II test was noted following routine, preventive maintenance procedures during which the hydrocarbon reactor column was replaced. As stated earlier, before-maintenance mean difference and standard deviation of the difference were +4.4 ppb and 7.5 ppb, respectively. Following replacement of the reactor, the mean increased to +20.1 ppb while the standard deviation remained essentially unchanged at 7.1 ppb. Responses to zero and span gases were nominal both before and after the replacement. Because of this change in performance, data from this analyzer were considered suspect and nonrepresentative of the average performance observed during the test. They have therefore been omitted from the computation of the "average" data.

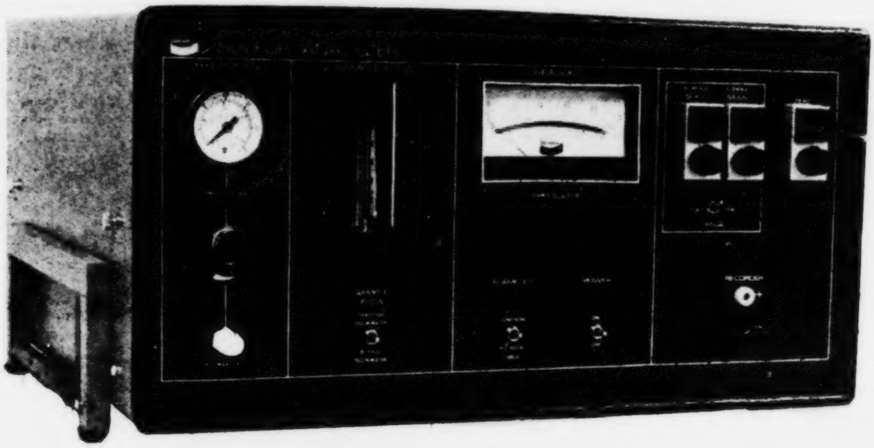


Figure 12. Bendix Model 8303 Sulfur Dioxide Analyzer (EQSA-1078-030). The Bendix Corporation Environmental and Process Instruments Division, P.O. Box 831, Louisburg, WV 24901.

General Description

The Bendix 8303 sulfur dioxide analyzer operates on the principle of flame photometric detection as described in Appendix A. It is equipped with a heated silver scrubber to remove ambient hydrogen sulfide, rendering the analyzer essentially specific for SO_2. Interference from other reduced sulfur compounds (e.g., methyl mercaptan) is possible but of minor significance at most monitoring sites. This scrubber is supplied in an independent module separate from the analyzer itself.

Because a silver scrubber has a tendency to convert H_2S to SO_2 in the presence of ozone, the analyzer incorporates an "ozone decomposer" stage prior to the silver scrubber. In this decomposer, ozone is removed from the sample stream by reaction with ethylene in a heated chamber. The ethylene is introduced into the sample stream by permeation from a small pressurized tank within the scrubber assembly.

The 8303 also includes a background sulfur addition device. A constant concentration of about 50 ppb of methyl mercaptan is added to the flame by permeation via the hydrogen supply. The purpose of this sulfur addition is to improve low-level sensitivity by improving the signal-to-noise ratio at very low SO_2 concentrations. It also avoids the potential problem of a hidden negative zero offset resulting from the inability of the electronics to process negative signals caused by negative zero drift.

To be used as an equivalent analyzer, the Model 8303 must be operated on a range of either 0 to 0.5 or 0 to 1.0 ppm, with a Teflon filter installed on the sample inlet of the H_2S scrubber assembly. Ambient air surrounding the analyzer must be within the range of 20° to 30° C, inclusive, and line voltage to the analyzer must be within the range of 105 to 125 Vac inclusive.

TABLE 5. BENDIX 8303 LABORATORY PERFORMANCE TEST RESULTS

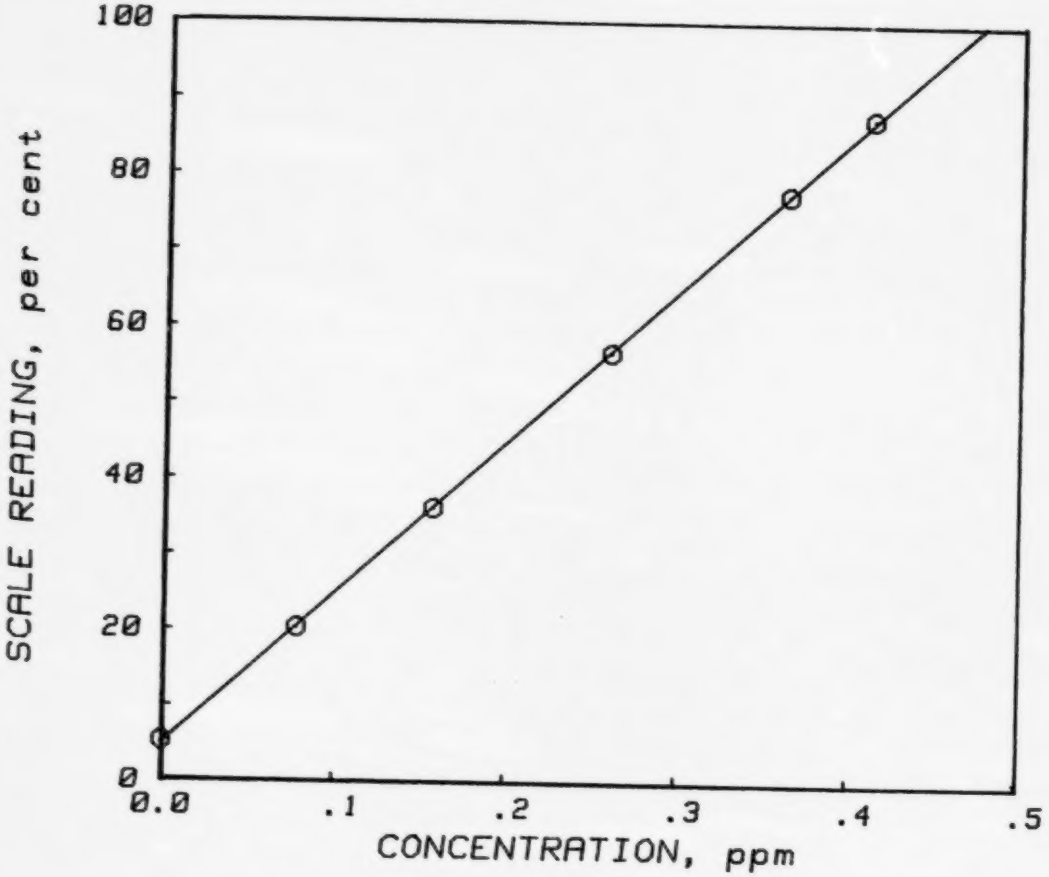
Performance parameters	Units	EPA specs.[a]	Manufacturer's test results[b]	EPA test results[c]
Noise – 0% URL	ppm	0.005	0.001	TESTING NOT YET PERFORMED
Noise – 80% URL	ppm	0.005	< 0.001	
Lower detectable limit	ppm	0.01	0.009	
Interferents	ppm			
CO_2		±0.02	- 0.002	
CO		±0.02	- 0.001	
O_3		±0.02	0.002	
H_2S		±0.02	0.002	
H_2O		±0.02	- 0.003	
Total		< 0.06	0.010[d]	
Zero drift – 12 h	ppm	±0.02	0.001[d]	
Zero drift – 24 h	ppm	±0.02	0.001[d]	
Span drift – 20% URL	%	±20.0	1.73[d]	
Span drift – 80% URL	%	±5.0	0.71[d]	
Lag time	min	20	0.3	
Rise time	min	15	0.3	
Fall time	min	15	0.3	
Precision – 20% URL	ppm	0.010	< 0.001	
Precision – 80% URL	ppm	0.015	0.001	

[a] From EPA equivalency regulations, 40 CFR Part 53.

[b] Average, from manufacturer's application for equivalency determination.

[c] Average, from EPA Phase I postdesignation tests.

[d] Average absolute values.



```
ANALYZER:    BENDIX         Y = MX + A       DATA:    X          Y
MODEL:       8303                                    ----       ----
SERIAL No.:  11252
POLLUTANT:   SO2            M =   199.721        1   0.000      5.300
RANGE:        .5 ppm         95% C.I.= ± 2.311   2    .078     20.300
LOCATION:    DAMDF                               3    .157     36.100
DATE:        03/30/79       A =     4.926        4    .260     56.600
DATE CODE:    79.089         95% C.I.= ±  .596   5    .363     77.400
NAME:        PHASE II                            6    .412     87.500
                            r =    .99997
```

Figure 13. Typical calibration curve for the Bendix 8303.

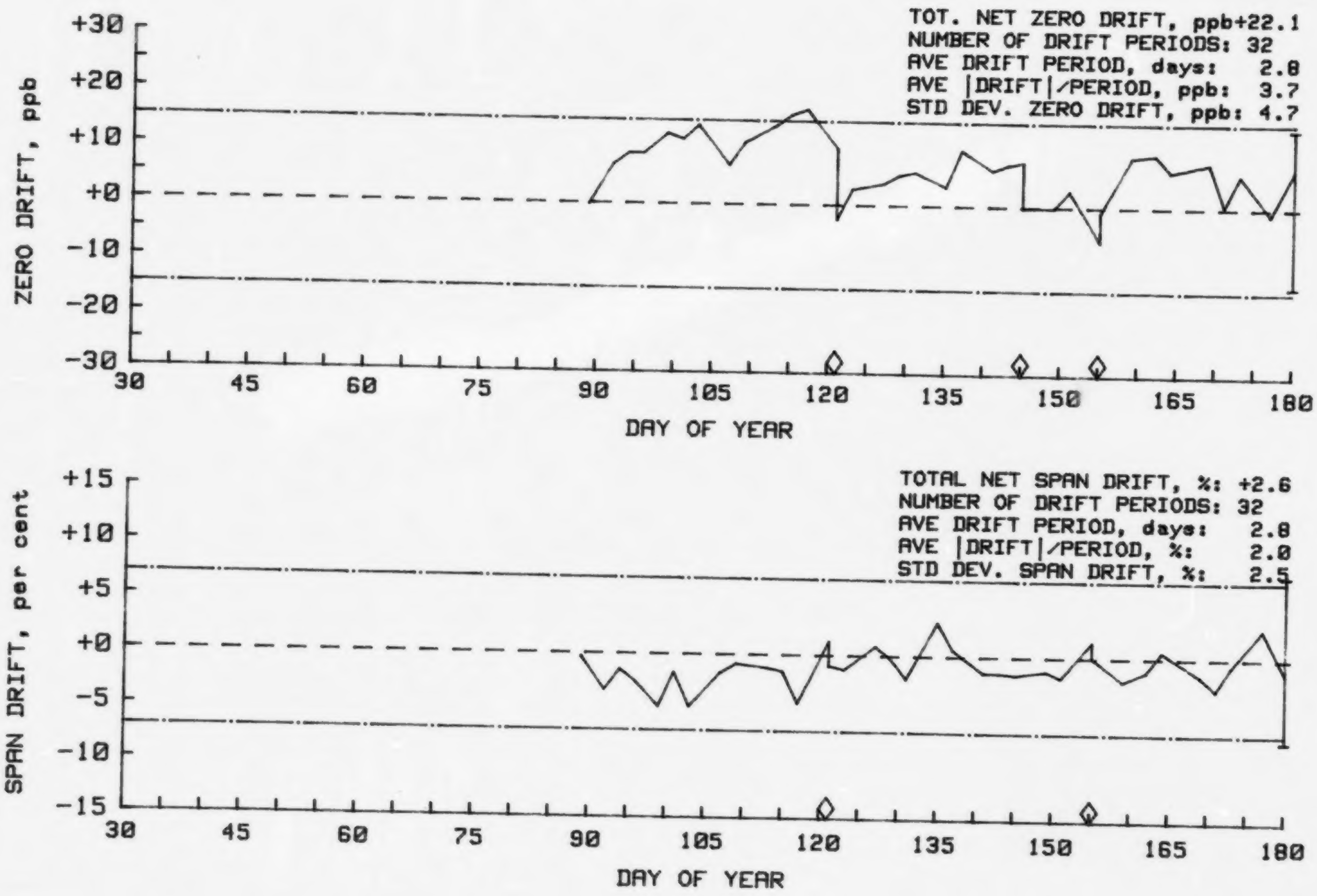


Figure 14. Zero and span drift in the Bendix 8303 SO_2 readings during the Phase II ambient monitoring test.

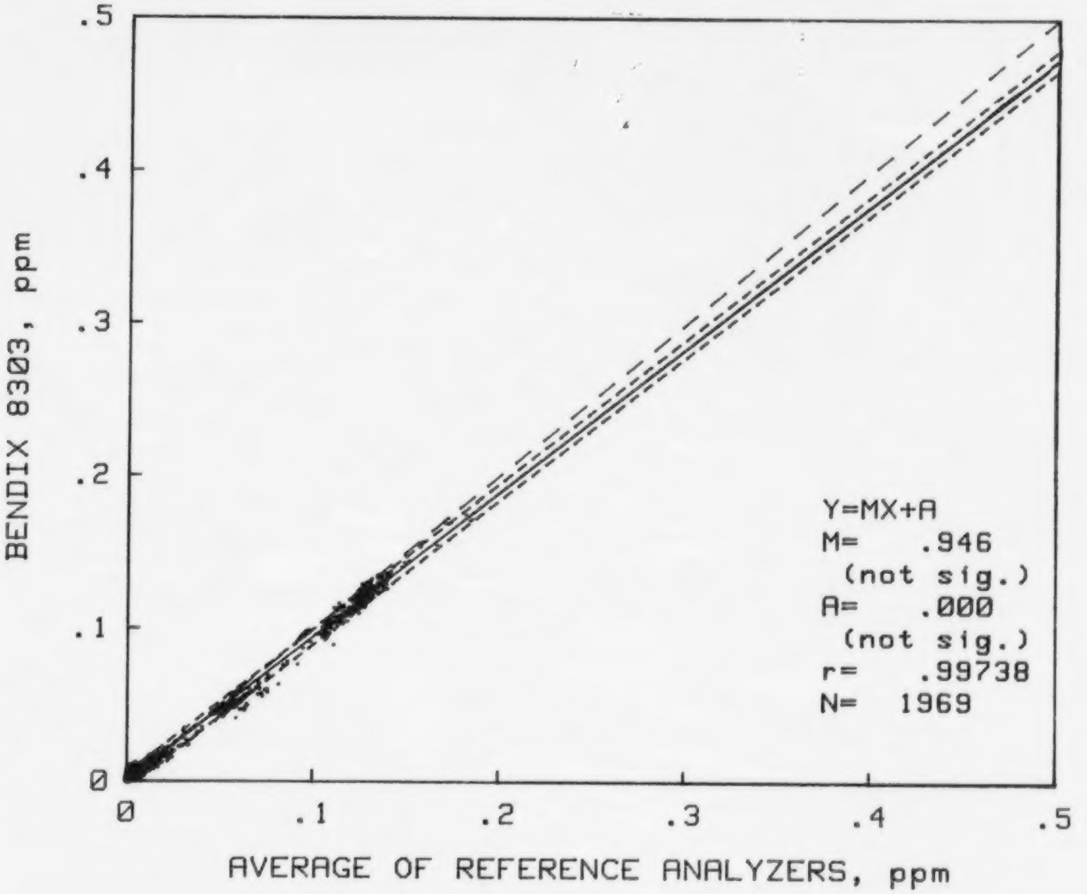
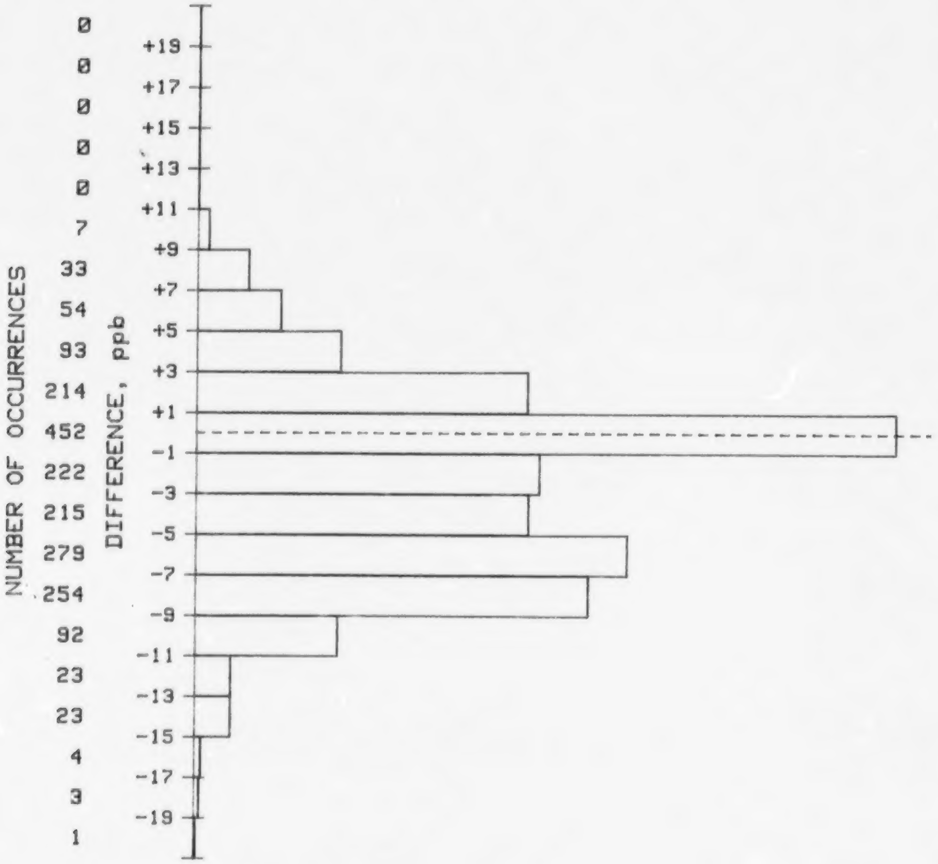
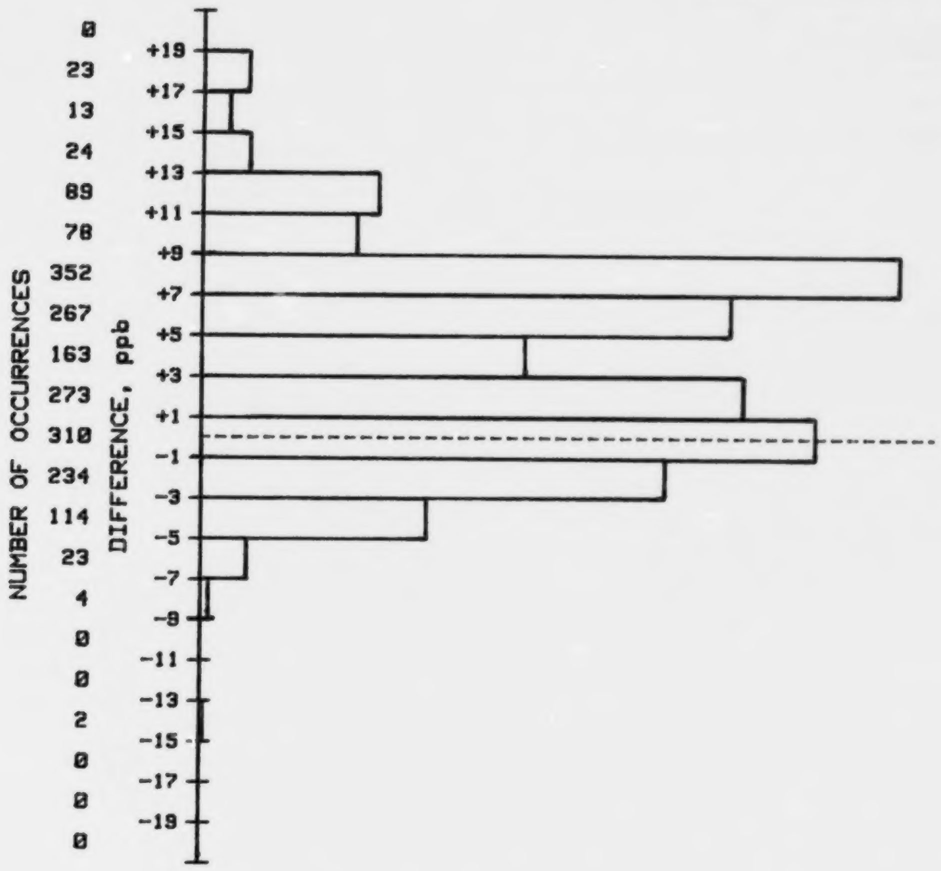


Figure 15. Relationship between the Bendix 8303 and the average of the other analyzers during the Phase II ambient monitoring test.



```
TOTAL No. OF DATA PAIRS:                 1969
CORRELATION COEFFICIENT:                    .997375
MEAN DIFFERENCE, ppb:                     -2.61
STD. DEVIATION OF DIFFERENCES, ppb:        4.6767
MAX. ABSOLUTE DIFFERENCE, ppb:            21
NO. ABSOLUTE DIFFERENCES >20:              1
```

Figure 16. Frequency distribution of differences in hourly SO_2 ambient air readings between the Bendix 8303 and the average of simultaneous readings from the other analyzers during the Phase II ambient monitoring test. All readings corrected for zero and span drift.



```
TOTAL No. OF DATA PAIRS:                   1969
CORRELATION COEFFICIENT:                       .997076
MEAN DIFFERENCE, ppb:                        +3.70
STD. DEVIATION OF DIFFERENCES, ppb:   4.9744
MAX. ABSOLUTE DIFFERENCE, ppb:          18
NO. ABSOLUTE DIFFERENCES >20:              0
```

Figure 17. Frequency distribution of differences in hourly SO_2 ambient air readings between the Bendix 8303 and the average of simultaneous readings from the other analyzers during the Phase II ambient monitoring test. Bendix 8303 readings are not corrected for zero and span drift.

Manufacturer's Recommended Maintenance

Operation	Frequency
Replace sample filter.	Monthly
Inspect dilution air filter.	Monthly
Service vacuum pump.	When vacuum is <23 in. Hg
Replace H_2 filter.	As required
Clean instrument.	As required
Leak check.	None specified
Flow check.	None specified
Check sulfur addition device.	None specified
Check scrubber permeation tank pressure.	None specified

Malfunctions

Factory checkout data could not be duplicated during the initial setup for Phase II.

General Comments

During initial startup of this analyzer on 2-14-79, the factory checkout data (flow rates, pressures, linearity, span, and zero) could not be duplicated. Bendix service personnel replaced the dilution air capillary and repeated the entire factory checkout procedure onsite. After the checkout, the analyzer was in operating condition.

During 130 days of Phase II testing, data were lost for 0 days.

Currently, Phase I testing has not been performed.

This instrument achieved equilibrium on span gases in 5 to 7 min.

The instrument manual maintenance instructions seemed incomplete in that many of the maintenance operations were described in detail, but no mention was made of when or under what conditions the operation was to be performed.

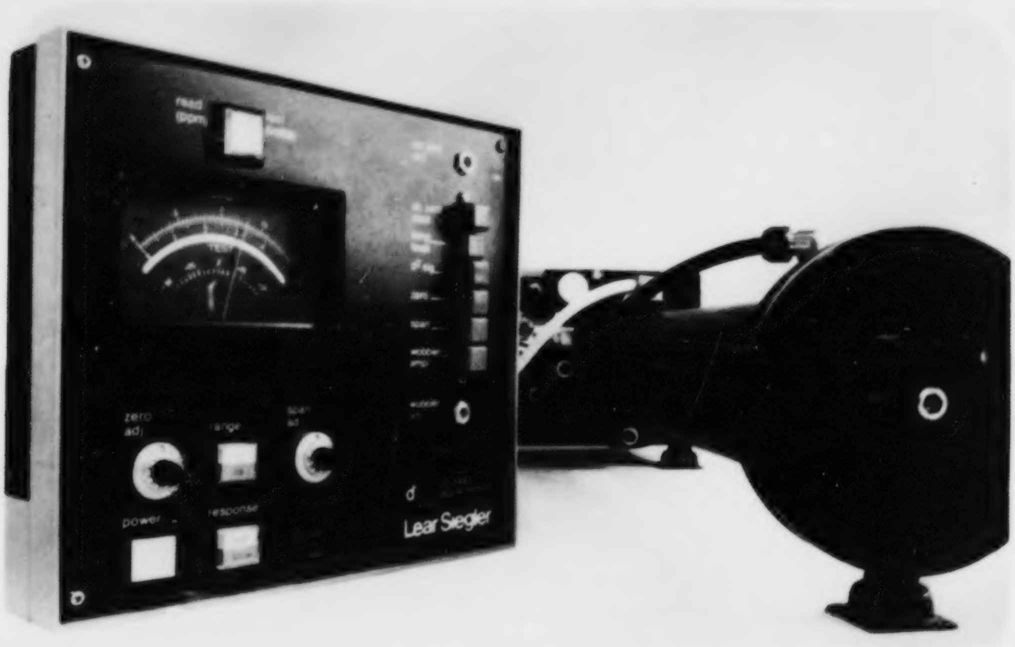


Figure 18. Lear Siegler SM1000 SO_2 Ambient Monitor (EQSA-1275-005). Lear Siegler, Inc., Environmental Technology Division, 74 Inverness Drive East, Englewood, CO 80112.

General Description

The Lear Siegler Model SM1000 sulfur dioxide analyzer is no longer in production, having been replaced by the Model AM2020. Some Model SM1000 analyzers are still in use, however, and are covered by this equivalent method designation. The Model SM1000 operates on the principle of second derivative spectroscopy as described in Appendix A. Use of the second derivative technique, along with judicious selection of the analytical wavelength, makes the analyzer specific for SO_2 without the need for chemical scrubbers or other conditioning. The analyzer is packaged in two separate modules, one containing the electronics and the other containing the optics and pneumatics. An optional outdoor enclosure is available for the analyzer, permitting it to be used over an extended temperature range of -34° to 38° C (-30° to 100° F).

To be used as an equivalent analyzer, the Model SM1000 must be operated on the 0-to-0.5-ppm range, at a wavelength of 299.5 nm, with the "slow" (300-second) response time, and with or without any of the following options:

- SM-1 Internal zero/span
- SM-2 Span timer card
- SM-3 0- to 0.1-volt output
- SM-4 0- to 5-volt output
- SM-5 Alternate sample pump
- SM-6 Outdoor enclosure.

Line voltage to the analyzer must be within the range of 105 to 125 Vac, inclusive.

TABLE 6. LEAR SIEGLER SM1000 LABORATORY PERFORMANCE TEST RESULTS

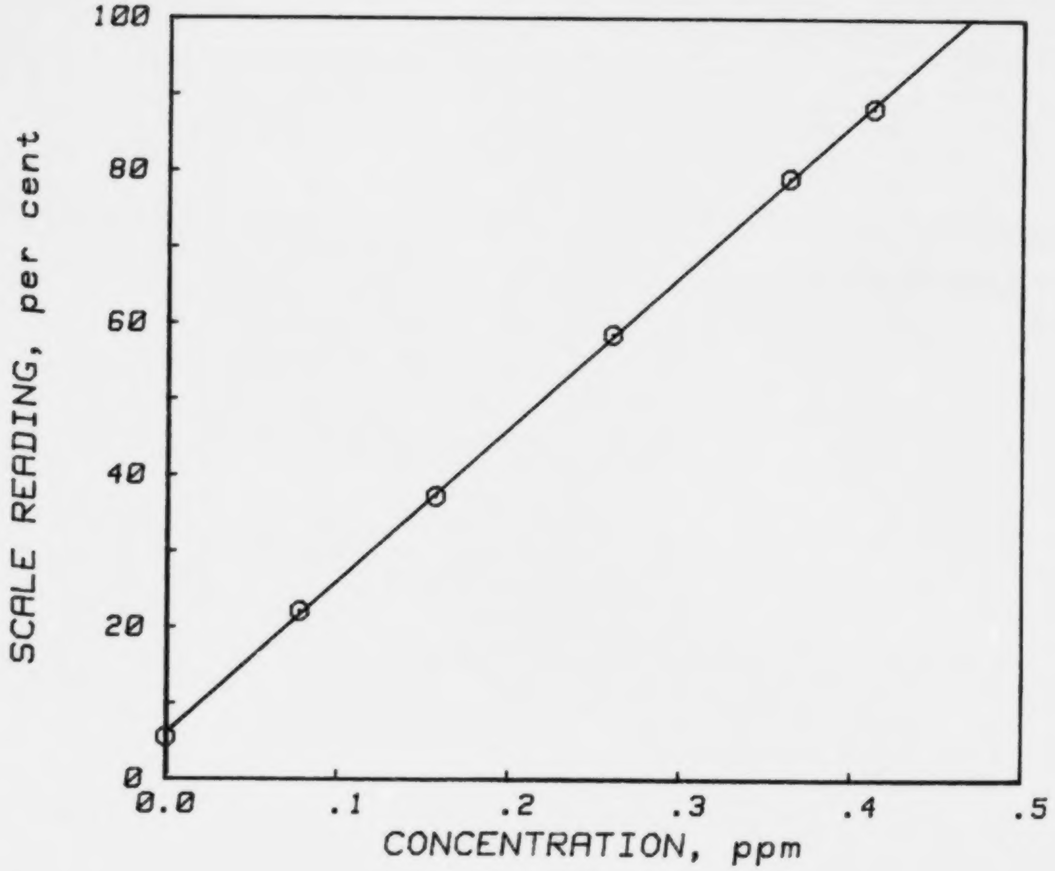
Performance parameters	Units	EPA specs.[a]	Manufacturer's test results[b]	EPA test results[c]
Noise – 0% URL	ppm	0.005	0.003	0.002
Noise – 80% URL	ppm	0.005	0.003	0.002
Lower detectable limits	ppm	0.01	0.013	0.010
Interferents	ppm			
Meta-xylene		±0.02	−0.002	−0.001
NO_2		±0.02	−0.001	−0.004
NO		±0.02	0.001	0.001
O_3		±0.02	0.002	−0.003
Total		≤0.06	0.006[d]	0.009[d]
Zero drift – 12 h	ppm	±0.02	0.018[d]	0.014[d]
Zero drift – 24 h	ppm	±0.02	0.004[d]	0.010[d]
Span drift – 20% URL	%	±20.0	3.98[d]	5.50[d]
Span drift – 80% URL	%	±5.0	0.86[d]	2.18[d]
Lag time	min	20	0.9	0.3
Rise time	min	15	8.4	7.5
Fall time	min	15	8.0	7.0
Precision – 20% URL	ppm	0.010	0.002	0.002
Precision – 80% URL	ppm	0.015	0.002	0.002

[a] From EPA equivalency regulations, 40 CFR Part 53.

[b] Average, from manufacturer's application for equivalency determination.

[c] Average, from EPA Phase I postdesignation tests.

[d] Average of absolute values.



```
ANALYZER:     LEAR SIEGLER     Y = MX + A        DATA:   X        Y
MODEL:        SM 1000                                   -----    -----
SERIAL No.:7564                                     1   0.000     5.500
POLLUTANT:    SO2              M =   200.722        2    .078    22.100
RANGE:         .5 ppm           95% C.I.= ± 3.597   3    .157    37.200
LOCATION:     DAMDF                                 4    .260    58.500
DATE:         03/30/79         A =      5.931       5    .363    79.000
DATE CODE:     79.089           95% C.I.= ±  .929   6    .412    88.200
NAME:         PHASE II
                               r =    .99992
```

Figure 19. Typical calibration curve for the Lear Siegler SM1000.

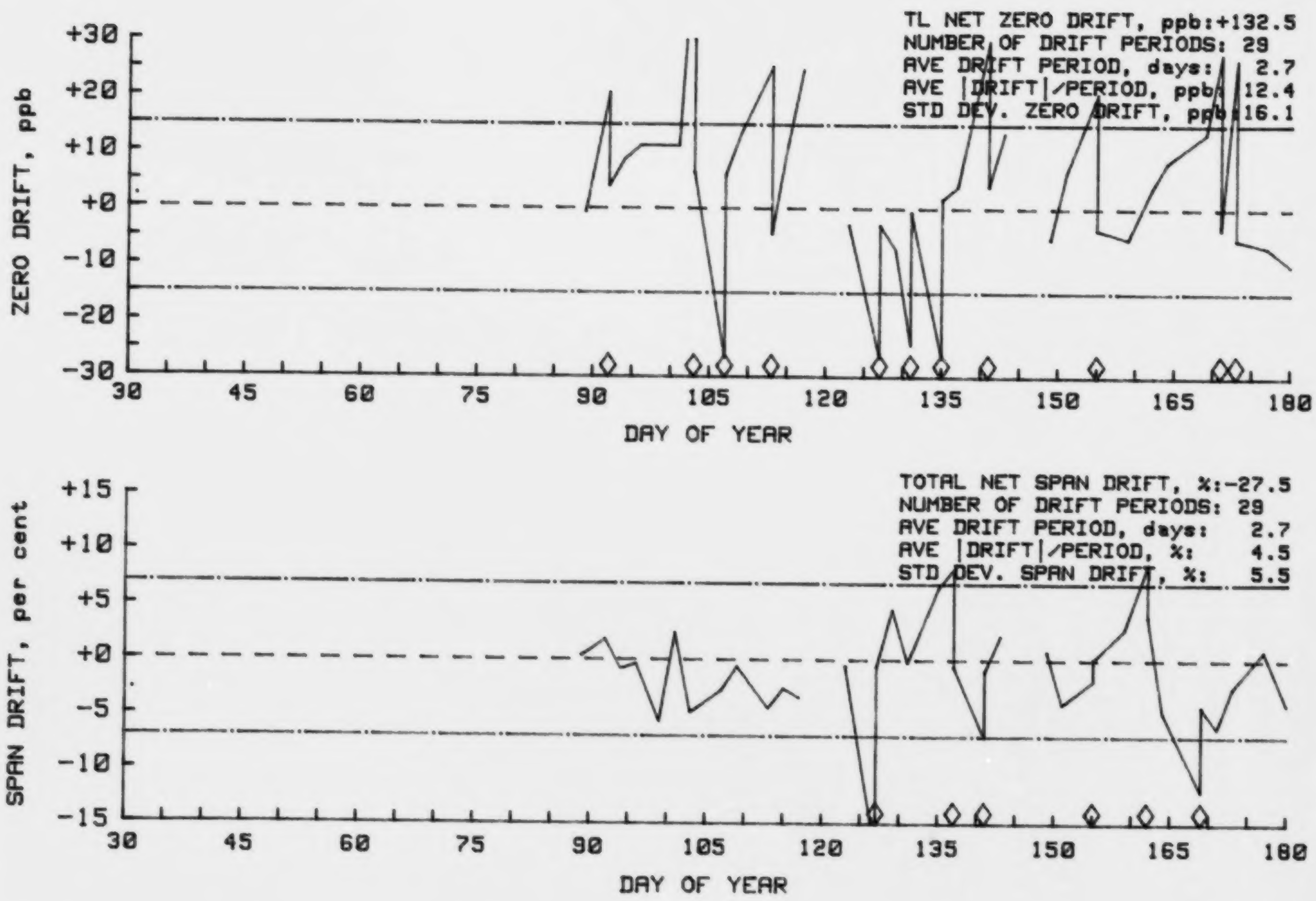


Figure 20. Zero and span drift in the Lear Siegler SM1000 SO_2 readings during the Phase II ambient monitoring test.

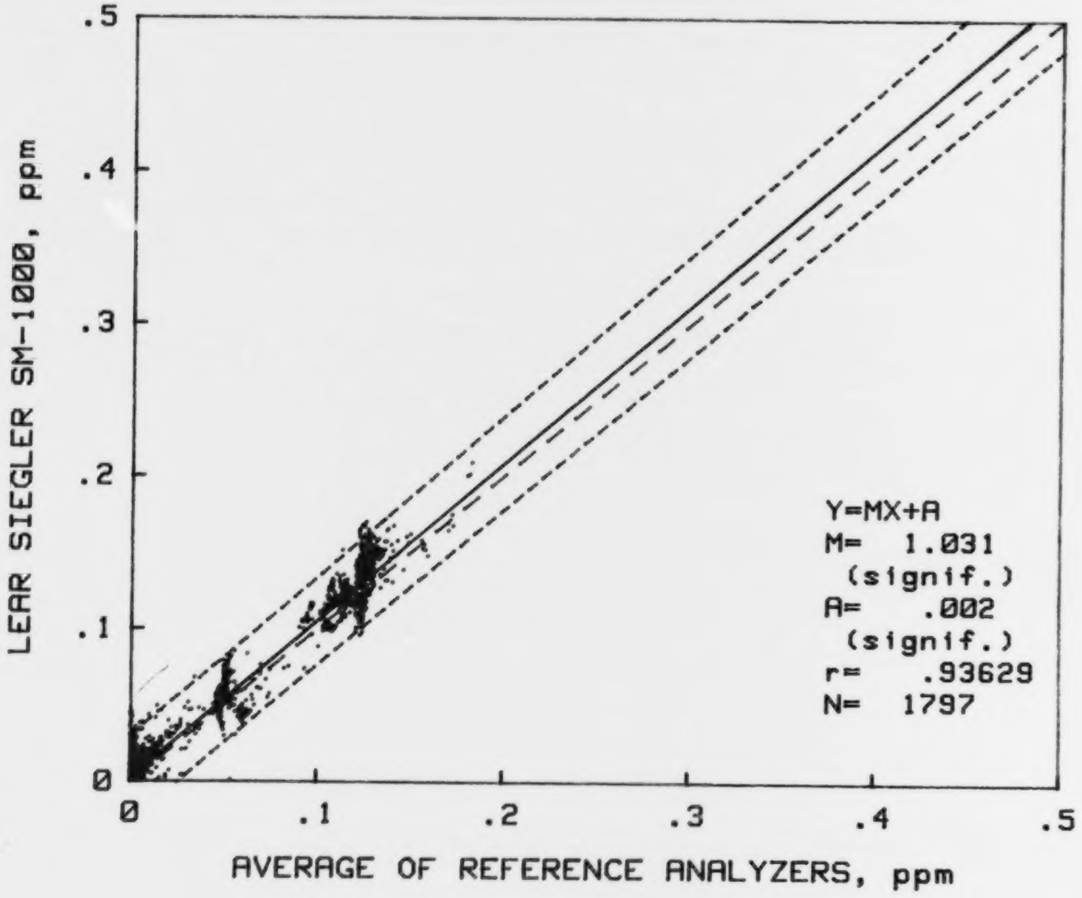
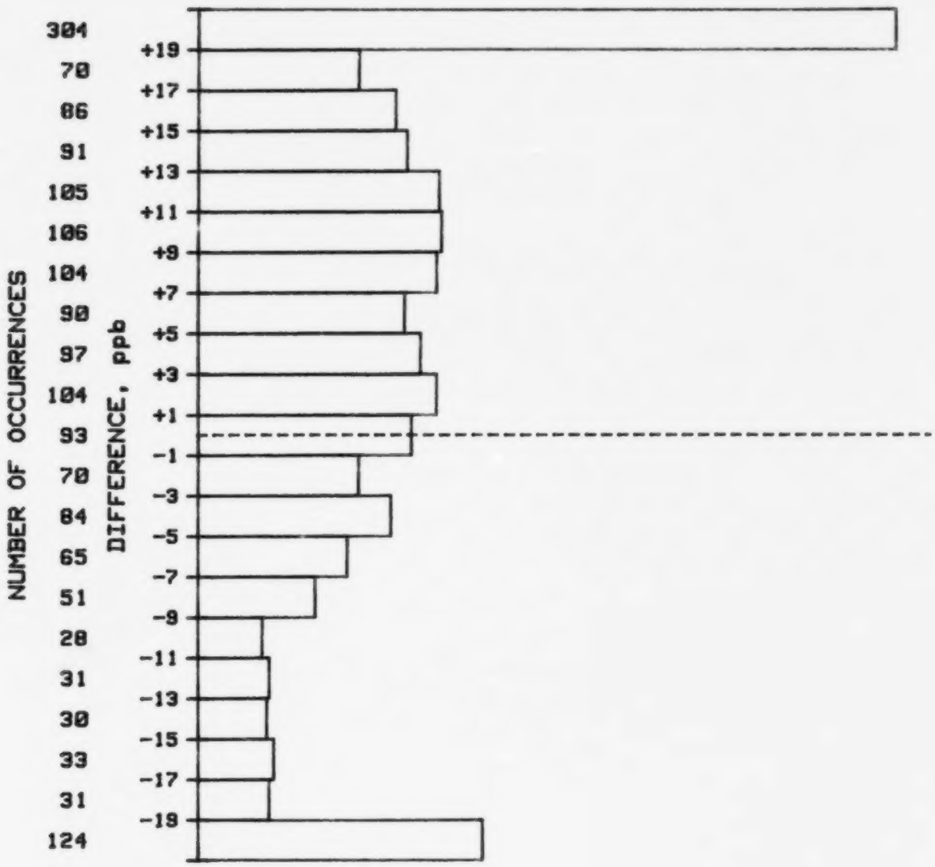
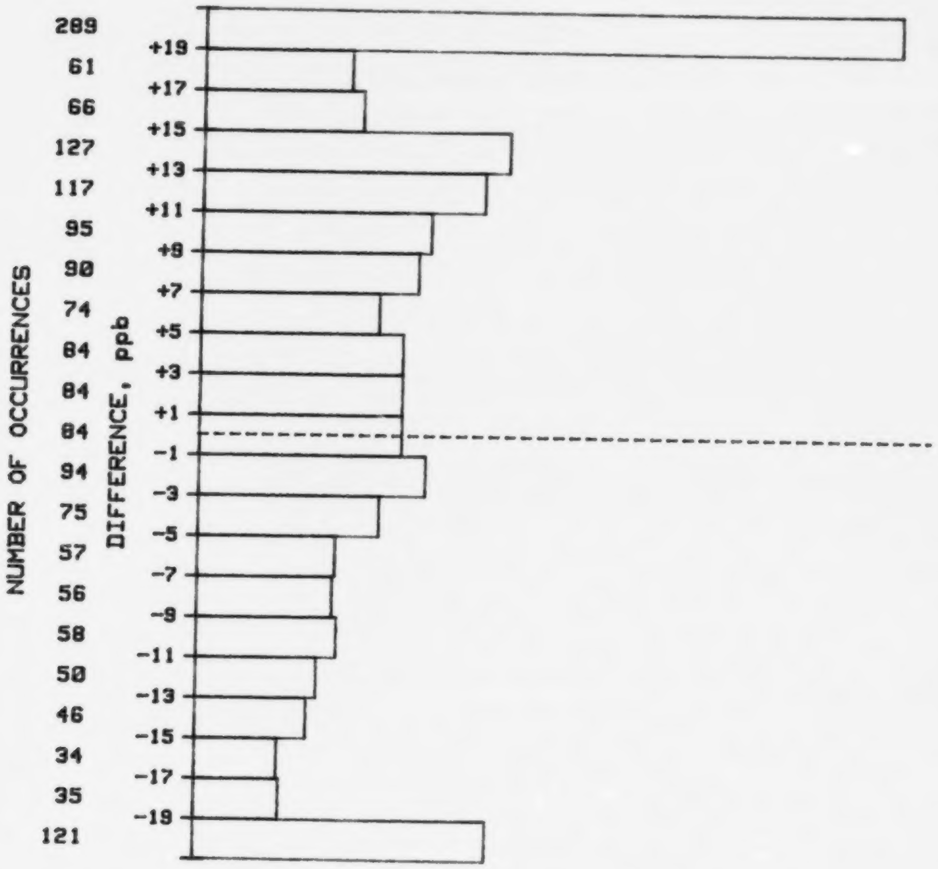


Figure 21. Relationship between the Lear Siegler SM1000 and the average of the other analyzers during the Phase II ambient monitoring test.



```
TOTAL No. OF DATA PAIRS:                   1797
CORRELATION COEFFICIENT:                       .936291
MEAN DIFFERENCE, ppb:                        +3.74
STD. DEVIATION OF DIFFERENCES, ppb:  20.7309
MAX. ABSOLUTE DIFFERENCE, ppb:         100
NO. ABSOLUTE DIFFERENCES >20:          390
```

Figure 22. Frequency distribution of differences in hourly SO_2 ambient air readings between the Lear Siegler SM1000 and the average of simultaneous readings from the other analyzers during the Phase II ambient monitoring test. All readings corrected for zero and span drift.



```
TOTAL No. OF DATA PAIRS:                    1797
CORRELATION COEFFICIENT:                         .924336
MEAN DIFFERENCE, ppb:                          +3.25
STD. DEVIATION OF DIFFERENCES, ppb:  21.0543
MAX. ABSOLUTE DIFFERENCE, ppb:          100
NO. ABSOLUTE DIFFERENCES >20:            377
```

Figure 23. Frequency distribution of differences in hourly SO_2 ambient air readings between the Lear Siegler SM1000 and the average of simultaneous readings from the other analyzers during the Phase II ambient monitoring test. Lear Siegler SM1000 readings are not corrected for zero and span drift.

Manufacturer's Recommended Maintenance

Operation	Frequency
Replace ultraviolet (UV) lamp.	Every 60 days
Clean sample cell mirrors.	Every 60 days
Replace zero air filters.	Every 60 days

Malfunctions

1-2-76 to 4-5-76	Excessive signal noise and drift.
4-5-76	Defective wobbler coil (returned to factory).
6-15-76 to 8-3-76	Signal noise and drift less severe but not acceptable.
9-21-76	Mirror alignment incorrect.
9-23-76 to 10-14-76	Excessive signal noise.
2-10-77 to 3-18-77	Excessive signal noise.
3-25-77	Analyzer lamp replaced.
11-1-78	Excessive signal noise--UV-tuned mirrors installed.
11-8-78	Analyzer lamp replaced.
11-20-78	Insufficient span pot.
11-27-78	Electronics corrected--span pot acceptable.
12-12-78	Excessive signal noise--power supply card replaced.
1-10-79	"Test" button light failed.
2-2-79	Negative response noted--analyzer taken off-line. Factory service requested.
2-7-79	Factory service personnel determined that the power supply was defective. New card ordered from factory.
3-27-79	New power supply card arrived and was installed--analyzer back on-line.
4-1-79 to 4-29-79	Signal noise steadily increased.

4-30-79	Analyzer optics cleaned and aligned. New lamp installed--signal noise substantially reduced.
5-23-79	Front panel fuse blew for no apparent reason.

General Comments

The instrument was set up initially in January 1976. Excessive drift and signal noise were unacceptable and persisted despite efforts to correct the problem, including mirror realignments, voltage adjustments, and routine zero and span checks. The instrument was returned to the factory for maintenance on 4-6-76. On 6-15-76, the instrument was received from the manufacturer and placed on-line. Drift continued to be a problem. The instrument was powered down on 8-3-76.

Phase I testing was to have begun on 9-21-76. However, it was delayed for 5 mo until excessive signal noise problems were corrected.

Between 5-3-77 and 11-3-78, the instrument was returned to the manufacturer for maintenance, repair, and application of the designation sticker.

On 11-3-78, in preparation for Phase II testing, new UV-tuned mirrors and a new lamp were installed.

Phase II testing was delayed for 18 days because of excessive signal noise.

On 4-30-79, corrective maintenance was performed in an attempt to reduce noise in the analyzer's response. The maintenance included:

- Cleaning the sample cell mirrors
- Cleaning the lamp lens
- Changing the UV lamp
- Aligning the sample cell mirrors
- Adjusting the analytical wavelength
- Peaking the optics.

Although maintenance required 6 h, the noise was reduced substantially.

During 194 days of Phase II testing, data were lost for 64 days because of malfunctions.

Phase II Testing Operator's Comment

This instrument repeatedly experienced malfunctions and required repair or adjustments. The instrument signal was characteristically noisy throughout the testing. At one point during the test, the anlyzer was off-line for 48 days awaiting arrival of a power supply board from the factory. The instrument manual was outdated. Several times, factory representatives either performed or suggested procedures other than those listed in the manual. The alignment of the mirrors was a difficult and time-consuming process. The recommended alignment procedure had to be performed in a dark room even though the instrument manual did not specify this condition. Any movement or vibration of the analyzer had the potential for upsetting the alignment of the optics.

The analyzer has a sample demand flow rate of 4.3 stdL/min. This demand rate is greater than the capability of many dynamic calibration systems at span concentrations of approximately 0.45 ppm.

Omission of Data from the Lear Siegler SM1000 in Computation of Averages Used for Phase II Comparisons

In the frequency distributions, each analyzer is compared to the average response from the other analyzers. Ideally, this average is assumed to represent the "real" or theoretical concentration of the sample. Nonrandom deviations (e.g., malfunctions or consistent bias) in any analyzer included in this averaging process would degrade the quality of the average and thus the entire comparison. Although it is not possible to eliminate nonrandom deviations completely, it is possible to eliminate or at least minimize obvious ones.

Throughout the Phase II test, the Lear Siegler SM1000 exhibited a higher standard deviation (s = 20.8 ppb) and a lower correlation coefficient (r = 0.934) than any of the other analyzers. This situation probably reflects the large amount of noise and variability constantly present in the analyzer's response. In addition, the analyzer experienced several malfunctions and required extensive repair and adjustment. Therefore, data from this instrument were considered nonrepresentative of the average concentrations observed during the test and have been omitted from computation of the "average" data.

Lear Siegler AM2020

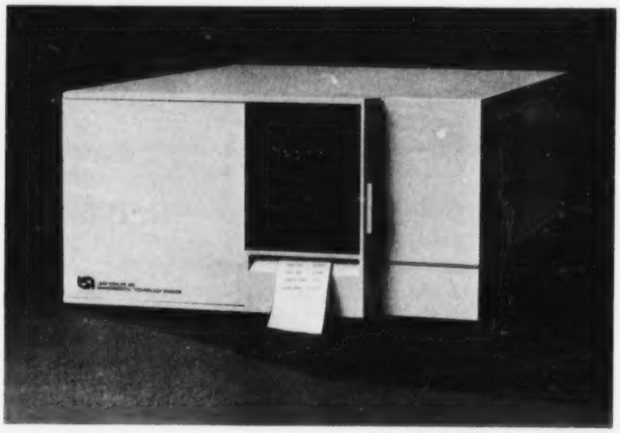


Figure 24. Lear Siegler Model AM2020 Ambient SO_2 Monitor (EQSA-1280-049). Lear Siegler, Inc., Environmental Technology Division, 74 Inverness Drive East, Englewood, CO 80112.

General Description

The Lear Siegler Model AM2020 sulfur dioxide analyzer operates on the principle of second derivative spectroscopy as described in Appendix A. Use of the second derivative technique, along with judicious selection of the analytical wavelength, makes the analyzer specific for SO_2 without the need for chemical scrubbers or other conditioning. The AM2020 differs from the SM1000 in that the modulation of the analytical wavelength required to measure the second derivative signal directly is accomplished by a continuously rotating "scanner" rather than a reciprocating mechanical slit.

Additionally, the AM2020 contains an on-board microprocessor that monitors and compensates for a variety of instrument conditions and performs diagnostic and self-testing operations.

To be used as an equivalent analyzer, the Model AM2020 must be operated on the 0-to-0.5- or the 0-to-1.0 ppm range, at a wavelength of 299.5 nm, with a 5-min integration period. Ambient air surrounding the analyzer must be within any 10° C temperature range between 20° and 45° C, inclusive. Line voltage to the analyzer must be within the range of 105 to 125 Vac, inclusive. The equivalent analyzer may be operated with or without the automatic zero and span correction feature.

TABLE 7. LEAR SIEGLER AM2020 LABORATORY PERFORMANCE TEST RESULTS

Performance parameters	Units	EPA specs.[a]	Manufacturer's test results[b]	EPA test results[c]
Noise – 0% URL	ppm	0.005	0.001	TESTING NOT YET PERFORMED
Noise – 80% URL	ppm	0.005	0.002	
Lower detectable limits	ppm	0.01	0.009	
Interferents	ppm			
Meta-xylene		±0.02	0.001	
NO_2		±0.02	−0.004	
NO		±0.02	< −0.001	
O_3		±0.02	−0.006	
Total		≤0.06	0.013[d]	
Zero drift – 12 h	ppm	±0.02	0.007[d]	
Zero drift – 24 h	ppm	±0.02	0.004[d]	
Span drift – 20% URL	%	±20.0	4.77[d]	
Span drift – 80% URL	%	±5.0	1.90[d]	
Lag time	min	20	0.5	
Rise time	min	15	5.0	
Fall time	min	15	5.1	
Precision – 20% URL	ppm	0.010	0.001	
Precision – 80% URL	ppm	0.015	0.003	

[a] From EPA equivalency regulations, 40 CFR Part 53.

[b] Average, from manufacturer's application for equivalency determination.

[c] Average, from EPA Phase I postdesignation tests.

[d] Average of absolute values.

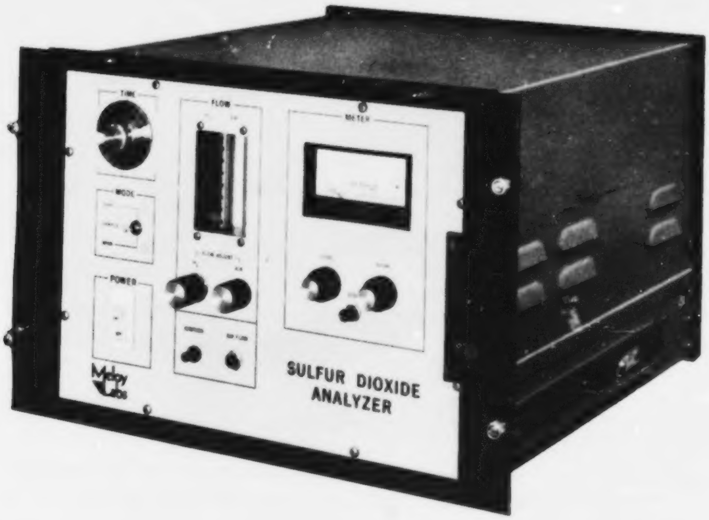


Figure 25. Meloy Model SA185-2A Sulfur Dioxide Analyzer (EQSA-1275-006). Columbia Scientific Industries, 11950 Jollyville Road, Austin, TX 78759.

General Description

The Meloy SA185-2A operates on the principle of flame photometric detection as described in Appendix A. It is equipped with a chemical scrubber to remove ambient hydrogen sulfide, making it practically specific for SO_2. Interference from other reduced sulfur compounds (e.g., methyl mercaptan) is possible but is usually of only minor significance at most ambient monitoring sites.

The standard output is exponential, following the characteristic of the flame photometric detector, but the analyzer may be equipped with a linear output option. This linear option, however, uses a logarithmic amplifier that by nature will not process negative signals. Therefore, any negative zero drift is truncated by the instrument output circuits, resulting in a zero output and a possibly nonapparent negative zero offset. Careful adjustment of the zero control is necessary to avoid such a negative zero offset.

To be used as an equivalent analyzer, the Model SA185-2A must be operated on the 0-to-0.5-ppm range, with or without any of the following options:

S-1	Linearized output
S-2	Modified recorder output
S-5	Teflon-coated block
S-6A	Reignite timer circuit
S-7	Press to read
S-11A	Manual zero and span
S-11B	Automatic zero and span
S-13	Status lights
S-14	Output booster amplifier
S-14B	Line transmitter board
S-18	Rack mount conversion
S-18A	Rack mount conversion
S-21	Front panel digital voltmeter
S-22	Remote zero/span control and status (timer)
S-22A	Remote zero/span control
S-23	Automatic zero adjust
S-23A	Automatic/manual zero adjust
S-24	Dual range linearized output
S-33	Remote range control and status (signals)
S-34	Remote control
S-35	Front panel digital meter with BCD output
S-36	Dual range log-linear output
S-38	Sampling mode status.

The analyzer may also be operated on the 0-to-1.0-ppm range; however, it must be equipped with option S-36 or options S-1 and S-24, with or without any of the other options. Ambient air surrounding the analyzer must be within the range of 20° to 30° C, inclusive, and line voltage must be within the range of 105 to 125 Vac, inclusive.

TABLE 8. MELOY SA185-2A LABORATORY PERFORMANCE TEST RESULTS

			Manufacturer's test results[b]		EPA test results[c]	
Performance parameters	**Units**	**EPA specs.[a]**	**Log**	**Linear**	**Log**	**Linear**
Noise – 0% URL	ppm	0.005	< 0.001	< 0.001	< 0.001	< 0.001
Noise – 80% URL	ppm	0.005	0.001	0.001	0.001	0.001
Lower detectable limit	ppm	0.01	0.007	0.007	0.005	0.005
Interferents	ppm					
O_3		±0.02	-0.001	-0.002	not tested	not tested
CO		±0.02	-0.001	-0.001	-0.003	-0.003
H_2O		±0.02	-0.004	-0.003	-0.001	-0.002
CO_2		±0.02	-0.010	-0.010	-0.025[d]	-0.026[d]
H_2S		±0.02	0.003	0.004	0.001	< 0.001
Total		≤ 0.06	0.019[e]	0.020[e]	0.030[e]	0.031[e]
Zero drift – 12 h	ppm	±0.02	0.001[e]	0.001[e]	< 0.001[e]	0.001[e]
Zero drift – 24 h	ppm	±0.02	0.001[e]	< 0.001[e]	0.002[e]	0.003[e]
Span drift – 20% URL	%	±20.0	2.84[e]	3.23[e]	0.98[e]	0.49[e]
Span drift – 80% URL	%	±5.0	2.16[e]	2.99[e]	0.65[e]	1.05[e]
Lag time	min	20	0.1	0.1	not tested	0.1
Rise time	min	15	1.1	1.1	not tested	0.7
Fall time	min	15	0.5	0.5	not tested	0.6
Precision – 20% URL	ppm	0.010	0.001	< 0.001	< 0.001	0.001
Precision – 80% URL	ppm	0.015	0.002	0.002	< 0.001	0.002

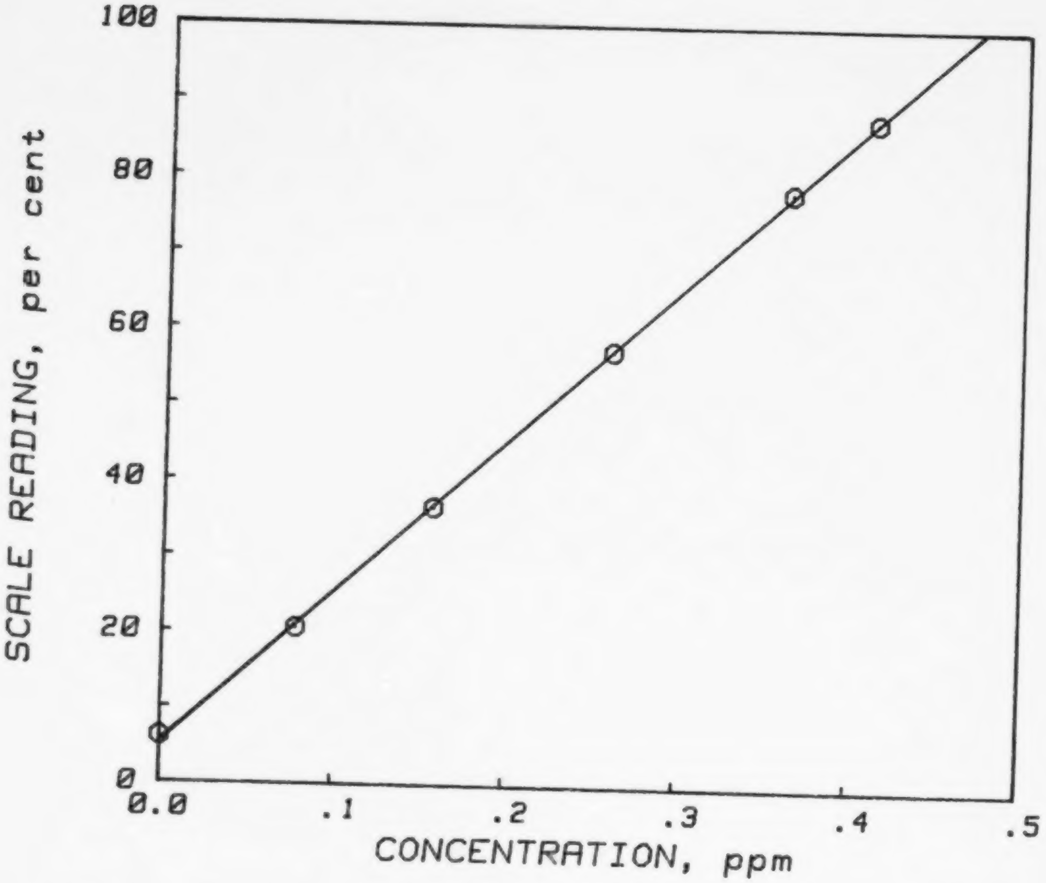
[a] From EPA equivalency regulations, 40 CFR Part 53.

[b] Average, from manufacturer's application for equivalency determination.

[c] Average, from EPA Phase I postdesignation tests, Serial Number 4HO24.

[d] See general comments.

[e] Average of absolute values.



ANALYZER: MELOY
MODEL: SA 185
SERIAL No.: 4H024
POLLUTANT: SO2
RANGE: .5 ppm
LOCATION: DAMDF
DATE: 03/30/79
DATE CODE: 79.089
NAME: PHASE II

Y = MX + A

M = 199.814
95% C.I.= ± 3.685

A = 5.456
95% C.I.= ± .951

r = .99991

DATA:	X	Y
1	0.000	6.100
2	.078	20.500
3	.157	36.500
4	.260	57.300
5	.363	78.300
6	.412	87.800

Figure 26. Typical calibration curve for the Meloy SA185-2A.

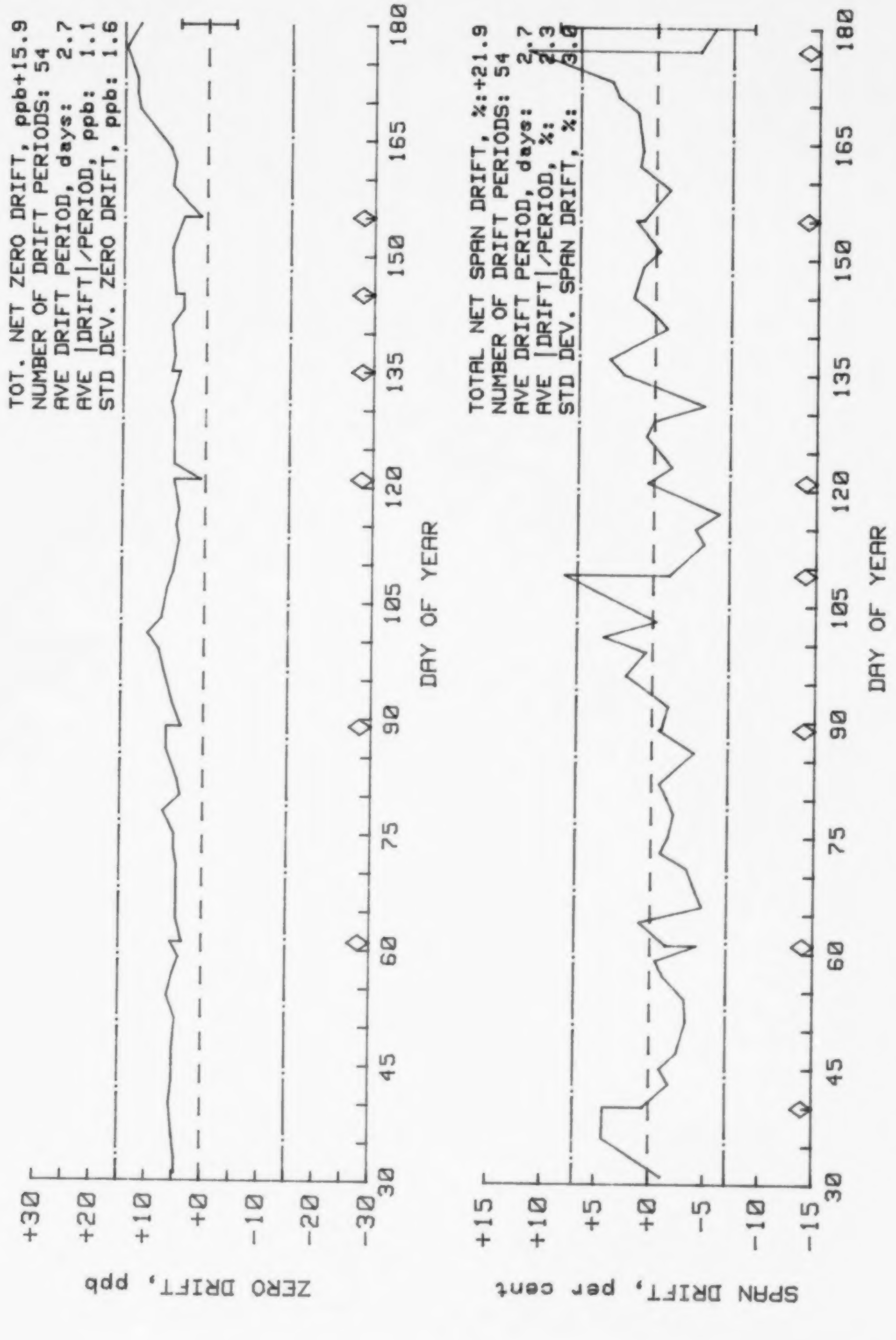


Figure 27. Zero and span drift in the Meloy SA185-2A SO_2 readings during the Phase II ambient monitoring test.

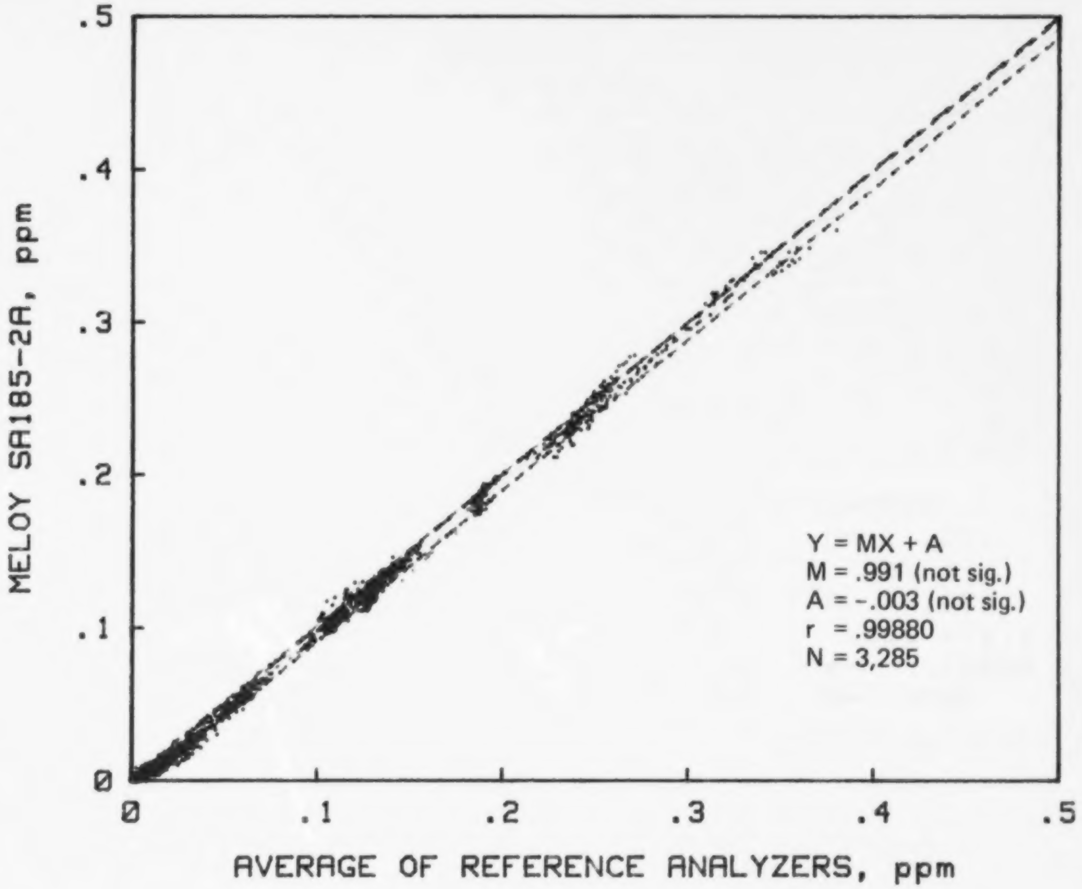
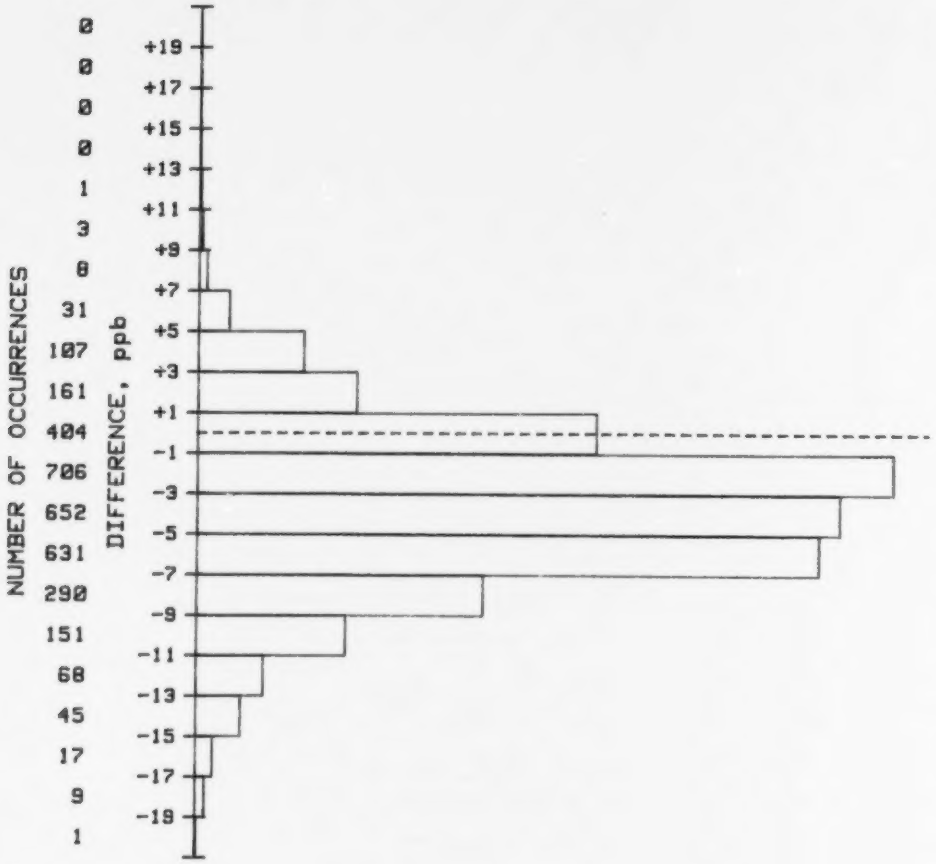
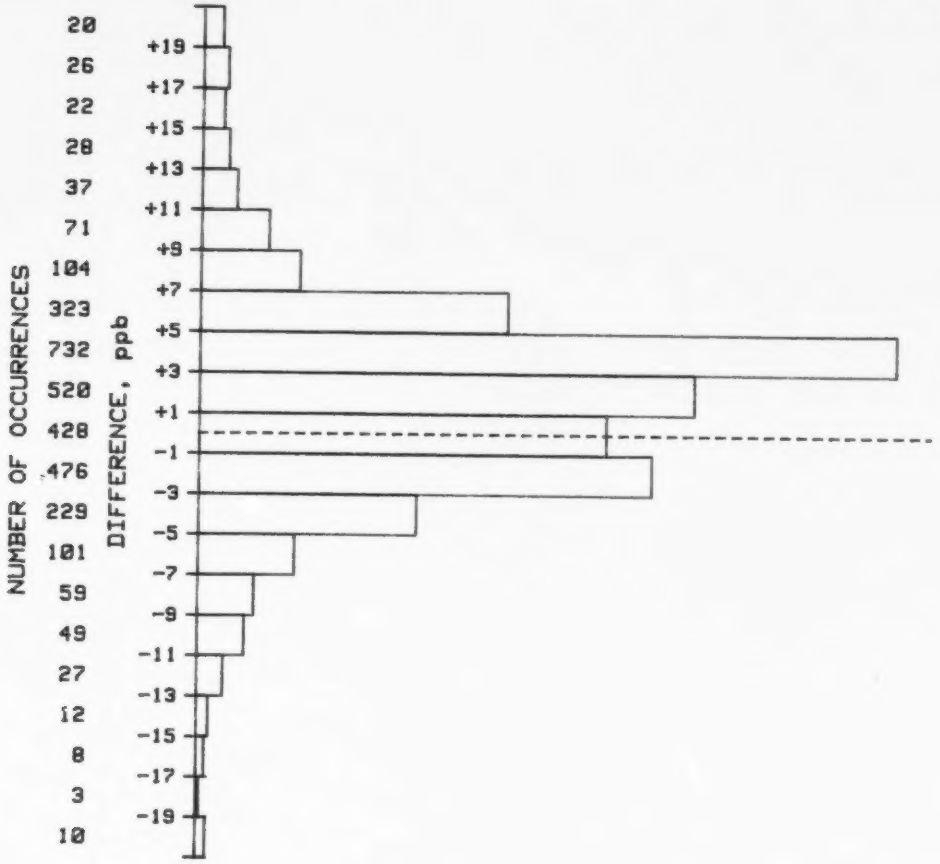


Figure 28. Relationship between the Meloy SA185-2A and the average of the other analyzers during the Phase II ambient monitoring test.



```
TOTAL No. OF DATA PAIRS:                3285
CORRELATION COEFFICIENT:                   .998796
MEAN DIFFERENCE, ppb:                    -3.81
STD. DEVIATION OF DIFFERENCES, ppb:       3.9524
MAX. ABSOLUTE DIFFERENCE, ppb:           20
NO. ABSOLUTE DIFFERENCES >20:             0
```

Figure 29. Frequency distribution of differences in hourly SO_2 ambient air readings between the Meloy SA185-2A and the average of simultaneous readings from the other analyzers during the Phase II ambient monitoring test. All readings corrected for zero and span drift.



```
TOTAL No. OF DATA PAIRS:                  3285
CORRELATION COEFFICIENT:                       .997855
MEAN DIFFERENCE, ppb:                        +1.58
STD. DEVIATION OF DIFFERENCES, ppb:           5.4001
MAX. ABSOLUTE DIFFERENCE, ppb:               28
NO. ABSOLUTE DIFFERENCES >20:                23
```

Figure 30. Frequency distribution of differences in hourly SO_2 ambient air readings between the Meloy SA185-2A and the average of simultaneous readings from the other analyzers during the Phase II ambient monitoring test. Meloy SA185-2A readings are <u>not corrected for zero and span drift</u>.

Manufacturer's Recommended Maintenance

Operation	Frequency
Replace charcoal filter.	Every 6 mo
Replace dilution air orifice.	Every 6 mo
Replace Teflon lines.	Annually
Replace flow restrictor capillary.	Annually
Clean rotameters.	Annually
Clean burner chamber.	Annually
Replace optical window.	Annually
Clean fan filter.	Annually
Replace H_2S scrubber cartridge.	Annually
Replace H_2 regulator.	Every 24 mo
Replace solenoid valves.	Every 24 mo
Replace vacuum pump.	Every 24 mo

Malfunctions

11-12-76	Phase I CO_2 interferent test failed (see general comments).
4-4-79	Pump diaphragm was replaced.

General Comments

On 11-12-76, during Phase I testing, the analyzer failed the CO_2 interferent test with an average interference equivalent of -0.026 ppm. Hydrogen flow was adjusted per conversations with a Meloy Laboratories representative. A second failure prompted Meloy to send a representative who adjusted the hydrogen flow and the oxygen content in the test atmosphere. The analyzer was never formally retested; however, after the adjustments, the analyzer did pass an informal test with an interference equivalent of approximately -18 to -19 ppb (specification: ±20 ppb). At this point, MSB personnel questioned whether or not this performance was representative of all Model SA185-2A analyzers, and Meloy representatives agreed to test 10 randomly chosen production units. All 10 of the units passed the tests with interference equivalents ranging from 10 to 18 ppb and averaging 14 ppb.

During Phase II testing, a special zero adjustment procedure was adopted to avoid the nonapparent negative zero drift possible with this analyzer. The zero setting was adjusted whenever the analyzer's front panel meter indicated a reading of less than zero while the analyzer was sampling zero gas. This adjustment procedure superseded the ±3 percent criterion applied to zero adjustments of the other analyzers in the test.

During Phase II testing, a misalignment in the analyzer's electronics caused the recorder to read 6.0 percent of chart when the analyzer front panel meter read zero. This occurred even though the recorder was zeroed at 5.0 percent of chart. The analyzer is equipped with circuits that allow this condition to be corrected. However, the condition was dealt with during the Phase II tests in the data reduction routines rather than by analyzer adjustment. Nevertheless, this misalignment was responsible for the consistent +5.0-ppb offset noted in the zero drift chart for this analyzer (Figure 27). The analysis of zero drift assumes a nominal zero of 5.0 percent of chart. A chart reading of 6.0 percent corresponds to +5.0 ppb.

During 215 days of Phase II testing, data were lost for 0 days because of malfunctions.

Phase II Testing Operator Comments

Signal noise levels at span concentrations were higher than the average noise experienced from the other analyzers during Phase II testing.

Engaging the locking mechanisms on the zero and span controls caused the zero/span settings to change, which was annoying at times.

Unlike most analyzers, the zero and span controls do not have graduated dials, which prohibited recording the control settings.

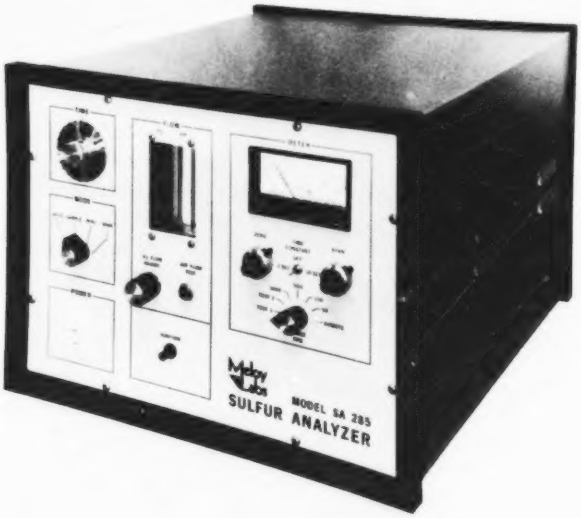


Figure 31. Meloy Model SA285E Sulfur Dioxide Analyzer (EQSA-1078-032). Columbia Scientific Industries, 11950 Jollyville Road, Austin, TX 78759.

General Description

The Meloy SA285E, a newer, improved version of the Model SA185-2A, operates on the flame photometric detection principle as described in Appendix A. It is equipped with a chemical scrubber to remove ambient hydrogen sulfide, making the analyzer essentially specific for SO_2. Interference from other reduced sulfur compounds such as methyl mercaptan is possible but of minor significance at most ambient monitoring sites. Linear output is standard on the SA285E, and it does not have the potential for nonapparent negative zero offset mentioned for the SA185-2A.

To be used as an equivalent analyzer, the Model SA285E must be operated on the following ranges and time constant switch positions:

Range, ppb	Time constant setting
0-50*	1 or 10
0-100*	1 or 10
0-500	Off, 1, or 10
0-1,000	Off, 1, or 10

The analyzer may be operated with or without any of the following options:

S-5	Teflon-coated block
S-14B	Line transmitter board
S-18	Rack mount conversion
S-18A	Rack mount conversion
S-21	Front panel digital meter
S-22	Remote zero/span control and status (timer)
S-22A	Remote zero/span control
S-22B	Remote zero/span control and status (pulse)
S-23	Auto zero adjust
S-23A	Auto/manual zero adjust
S-25	Press to read
S-26	Manual zero and span
S-27	Auto manual zero/span
S-28	Auto range and status
S-30	Auto reignite
S-32	Remote range control and status
S-35	Front panel digital meter with BCD output
S-37	Temperature status lights
S-38	Sample mode status.

Ambient air surrounding the analyzer must be within the range of 10° to 40° C, inclusive, and line voltage to the analyzer must be within the range of 105 to 130 Vac, inclusive.

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*Designation of ranges less than 500 ppb is based on meeting the same absolute performance specifications required for the 0-to-500-ppb range; proportionately more restrictive performance specifications applicable to lower ranges have not been established.

TABLE 9. MELOY SA285E LABORATORY PERFORMANCE TEST RESULTS

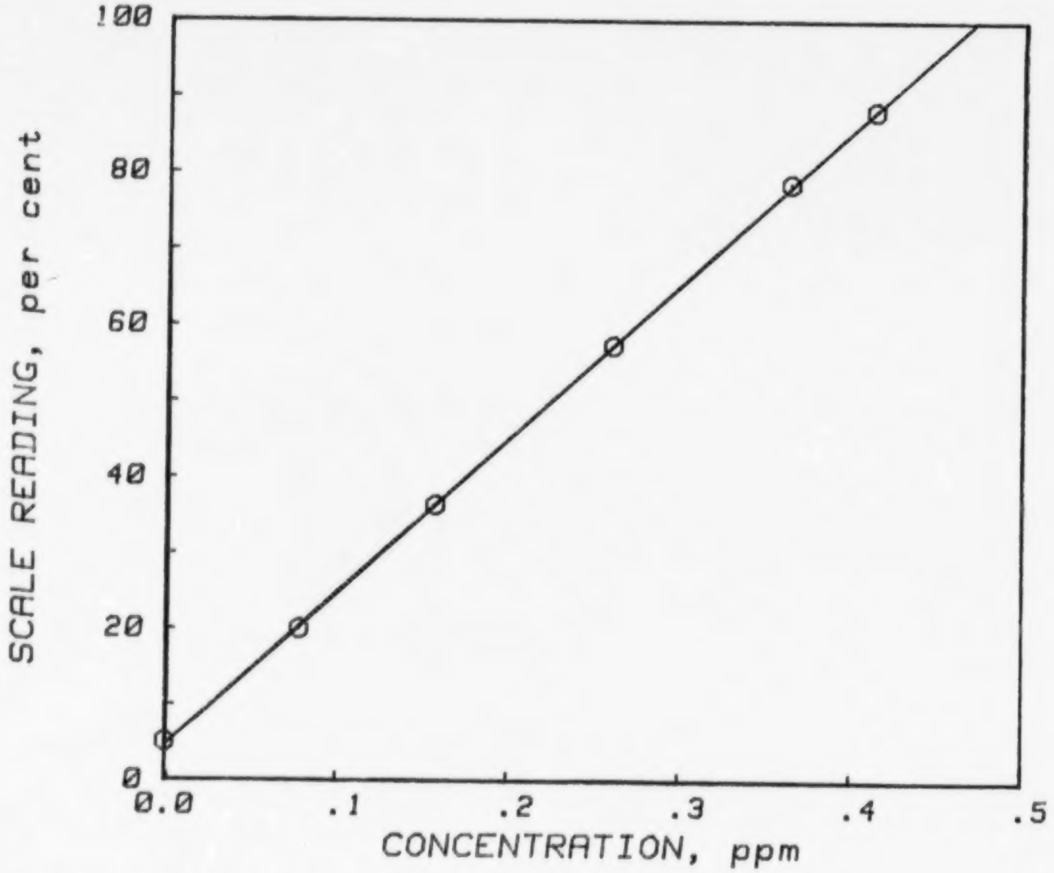
Performance parameters	Units	EPA specs.[a]	Manufacturer's test results[b]	EPA test results[c]
Noise – 0% URL	ppm	0.005	< 0.001	TESTING NOT YET PERFORMED
Noise – 80% URL	ppm	0.005	0.001	
Lower detectable limit	ppm	0.01	0.009	
Interferents	ppm			
CO_2		±0.02	−0.014	
CO		±0.02	−0.001	
H_2O		±0.02	−0.001	
H_2S		±0.02	0.004	
O_3		±0.02	−0.002	
Total		< 0.06	0.022[d]	
Zero drift – 12 h	ppm	±0.02	0.001[d]	
Zero drift – 24 h	ppm	±0.02	0.002[d]	
Span drift – 20% URL	%	±20.0	2.25[d]	
Span drift – 80% URL	%	±5.0	1.22[d]	
Lag time	min	20	< 0.1	
Rise time	min	15	0.8	
Fall time	min	15	0.4	
Precision – 20% URL	ppm	0.010	< 0.001	
Precision – 80% URL	ppm	0.015	0.002	

[a] From EPA equivalency regulations, 40 CFR Part 53.

[b] Average, from manufacturer's application for equivalency determination.

[c] Average, from EPA Phase I postdesignation tests.

[d] Average of absolute values.



ANALYZER: MELOY
MODEL: SA 285 E
SERIAL No.: 7E140
POLLUTANT: SO2
RANGE: .5 ppm
LOCATION: DAMDF
DATE: 03/30/79
DATE CODE: 79.089
NAME: PHASE II

Y = MX + A

M = 202.713
95% C.I.= ± 2.776

A = 4.642
95% C.I.= ± .717

r = .99995

DATA:	X	Y
1	0.000	5.100
2	.078	20.000
3	.157	36.300
4	.260	57.300
5	.363	78.500
6	.412	88.100

Figure 32. Typical calibration curve for the Meloy SA285E.

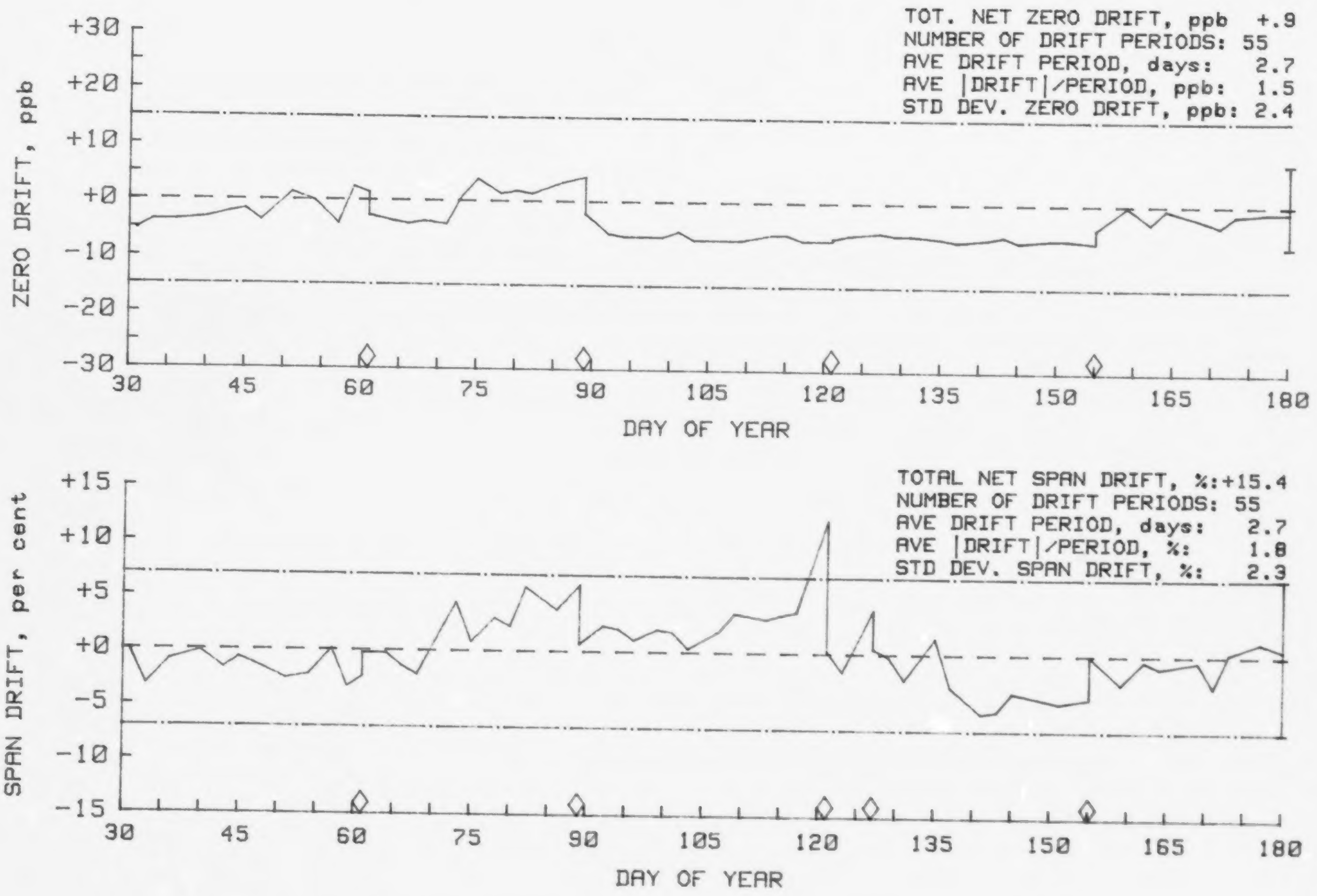


Figure 33. Zero and span drift in the Meloy SA285E SO_2 readings during the Phase II ambient monitoring test.

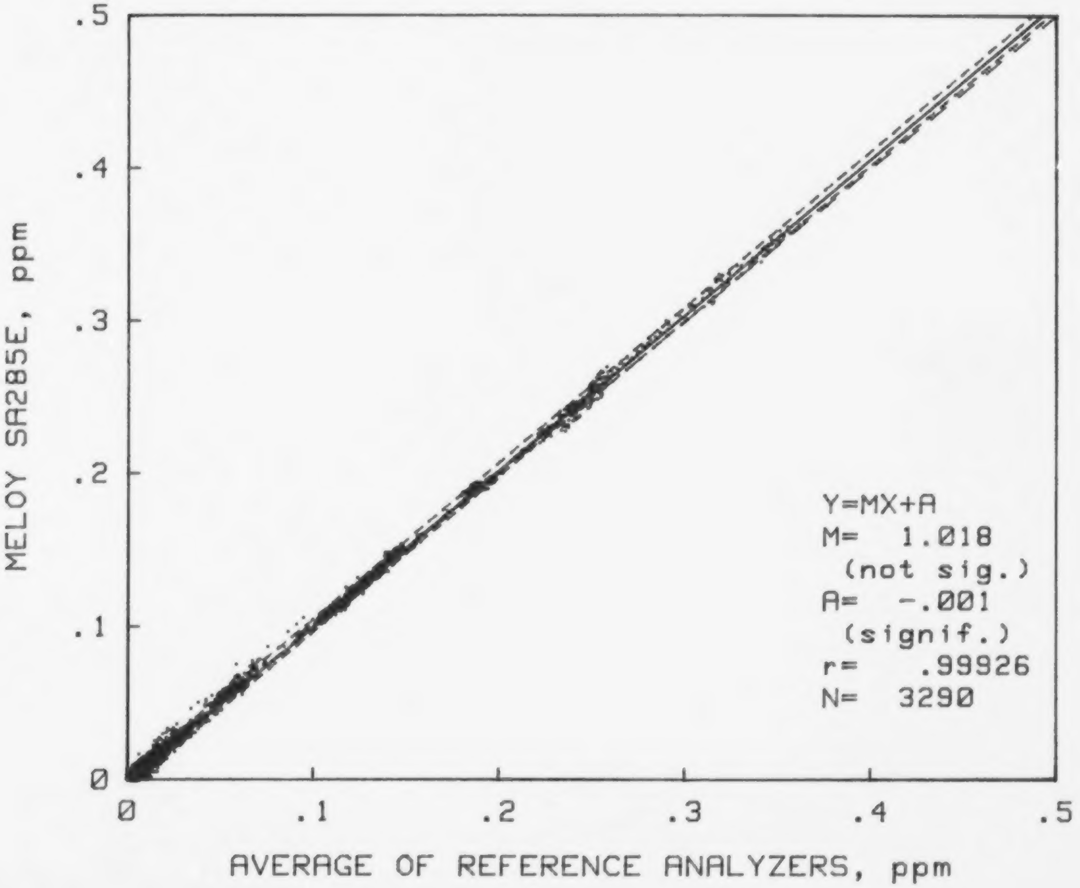
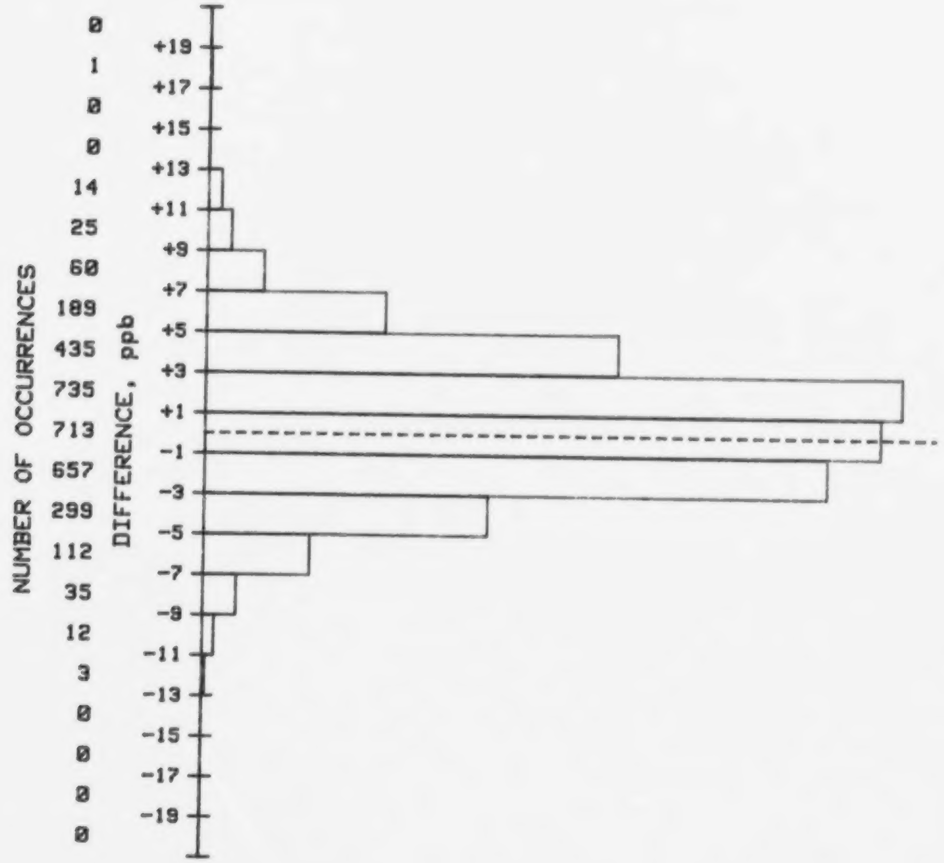
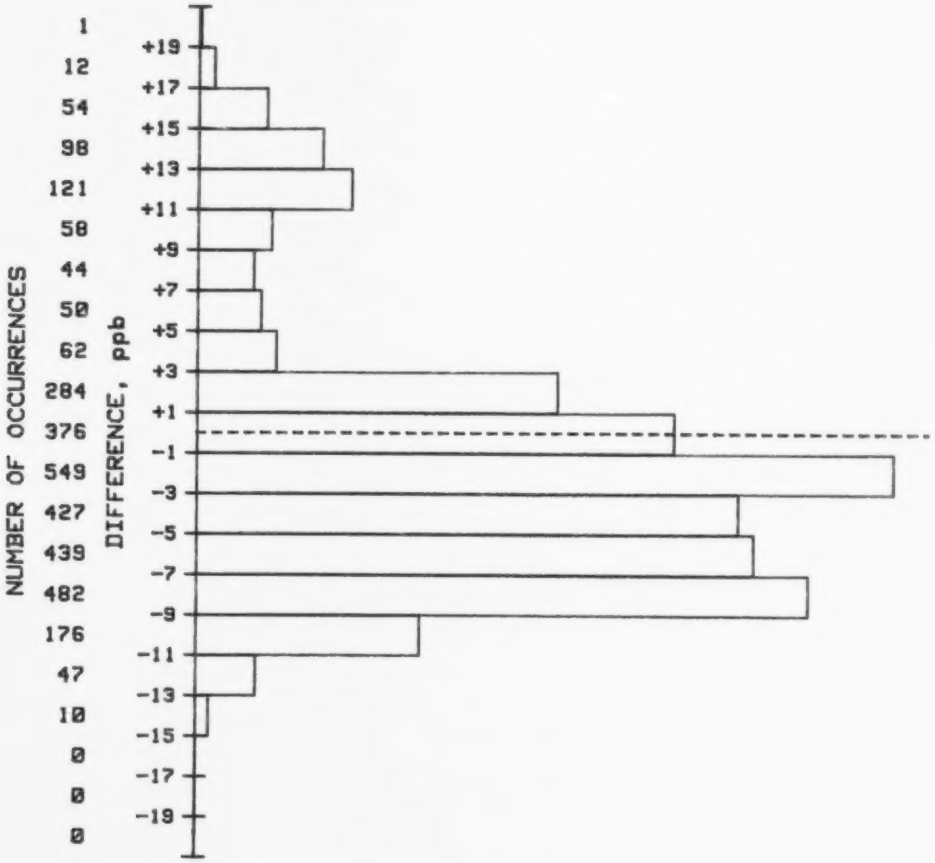


Figure 34. Relationship between the Meloy SA285E and the average of the other analyzers during the Phase II ambient monitoring test.



```
TOTAL No. OF DATA PAIRS:                      3290
CORRELATION COEFFICIENT:                          .999261
MEAN DIFFERENCE, ppb:                           +.50
STD. DEVIATION OF DIFFERENCES, ppb:    3.4297
MAX. ABSOLUTE DIFFERENCE, ppb:             17
NO. ABSOLUTE DIFFERENCES >20:               0
```

Figure 35. Frequency distribution of differences in hourly SO_2 ambient air readings between the Meloy SA285E and the average of simultaneous readings from the other analyzers during the Phase II ambient monitoring test. All readings corrected for zero and span drift.



TOTAL No. OF DATA PAIRS: 3290
CORRELATION COEFFICIENT: .998228
MEAN DIFFERENCE, ppb: -1.75
STD. DEVIATION OF DIFFERENCES, ppb: 6.4814
MAX. ABSOLUTE DIFFERENCE, ppb: 21
NO. ABSOLUTE DIFFERENCES >20: 1

Figure 36. Frequency distribution of differences in hourly SO_2 ambient air readings between the Meloy SA285E and the average of simultaneous readings from the other analyzers during the Phase II ambient monitoring test. Meloy SA285E readings are not corrected for zero and span drift.

Manufacturer's Recommended Maintenance

Operation	Frequency
Replace exhaust filter.	Every 3 mo
Replace zero air filter.	Every 3 mo
Replace Teflon sample line.	Annually
Clean rotameters.	Annually
Rebuild vacuum pump.	Annually
Replace H_2S scrubber.	Annually
Clean burner chamber.	Annually
Replace optical window.	Annually
Clean exhaust orifice.	Annually
Clean dilution orifice.	Annually
Clean chassis.	Annually
Clean fan.	Annually
Clean fan filter.	Annually
Replace H_2 filter (if necessary).	Annually
Replace flow capillary (if necessary).	Every 24 mo
Replace H_2 regulator.	Every 24 mo
Replace solenoid valves.	Every 24 mo

Malfunctions

12-11-78	H_2 filter was clogged (see General Comments)

General Comments

On 12-11-78, during a routine Phase II zero/span check, it was noted that the analyzer H_2 flow rate had decreased significantly while the air flow rate had increased significantly. The dilution air orifice was cleaned and, per the manufacturer's recommendation, the H_2 filter assembly (a sintered frit that was badly clogged) was removed. The removal of the H_2 filter corrected both flow rate problems, and normal operation was resumed. A new filter assembly was ordered; it arrived and was installed on 2-26-79.

During 215 days of Phase II testing, data were lost for 0 days because of malfunctions.

Currently, Phase I testing has not been performed.

Phase II Testing Operator's Comments

This analyzer achieved equilibrium on span gases in less than 15 min.

The voltage test modes featured in this analyzer serve as convenient quality control checks on the day-to-day condition of the instrument's electronics.

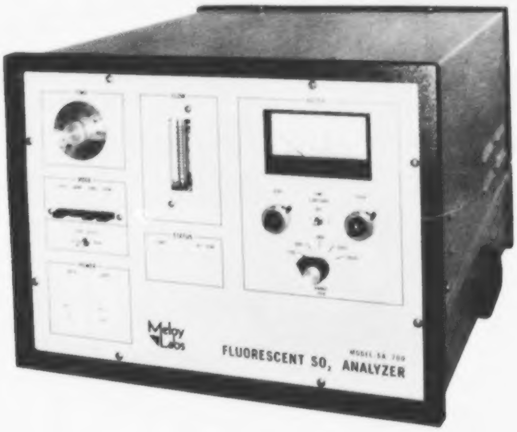


Figure 37. Meloy Model SA700 Fluorescence Sulfur Dioxide Analyzer (ESQA-0580-046). Columbia Scientific Industries, 11950 Jollyville Road, Austin, TX 78759.

General Description

The Meloy Model SA700 fluorescence sulfur dioxide analyzer operates on the principle of fluorescence as described in Appendix A. It differs from many fluorescence-type analyzers in that the source UV radiation is continuous rather than modulated by mechanical chopping or electronic pulsing. The analyzer is equipped with a temperature-controlled scrubber to remove aromatic hydrocarbons from the sample that would otherwise produce a positive interference with the fluorescence technique. Removal of ambient moisture from the sample is effected by a permeation-type dryer, although moisture removal is not required for interference rejection due to judicious selection of the excitation wavelength that minimizes the effect of this potential interferent.

To be used as an equivalent analyzer, the Model SA700 must be operated on the 0-to-250,* 0-to-500, or the 0-to-1,000-ppb range with a time constant switch position of either 2 or 3, with or without any of the following options:

---

*Designation of ranges less than 500 ppb is based on meeting the same absolute performance specifications required for the 0-to-500-ppb range; proportionately more restrictive performance specifications applicable to lower ranges have not been established.

FS-1	Current output
FS-2	Rack mount conversion
FS-2A	Rack mount conversion
FS-2B	Rack mount conversion
FS-3	Front panel mounted digital meter
FS-5	Auto/manual zero/span with status
FS-6	Remote/manual zero/span with status
FS-7	Auto zero adjust.

Ambient air surrounding the analyzer must be within the range of 20° to 30° C, inclusive, and line voltage to the analyzer must be within the range of 105 to 130 Vac, inclusive.

TABLE 10. MELOY SA700 LABORATORY PERFORMANCE TEST RESULTS

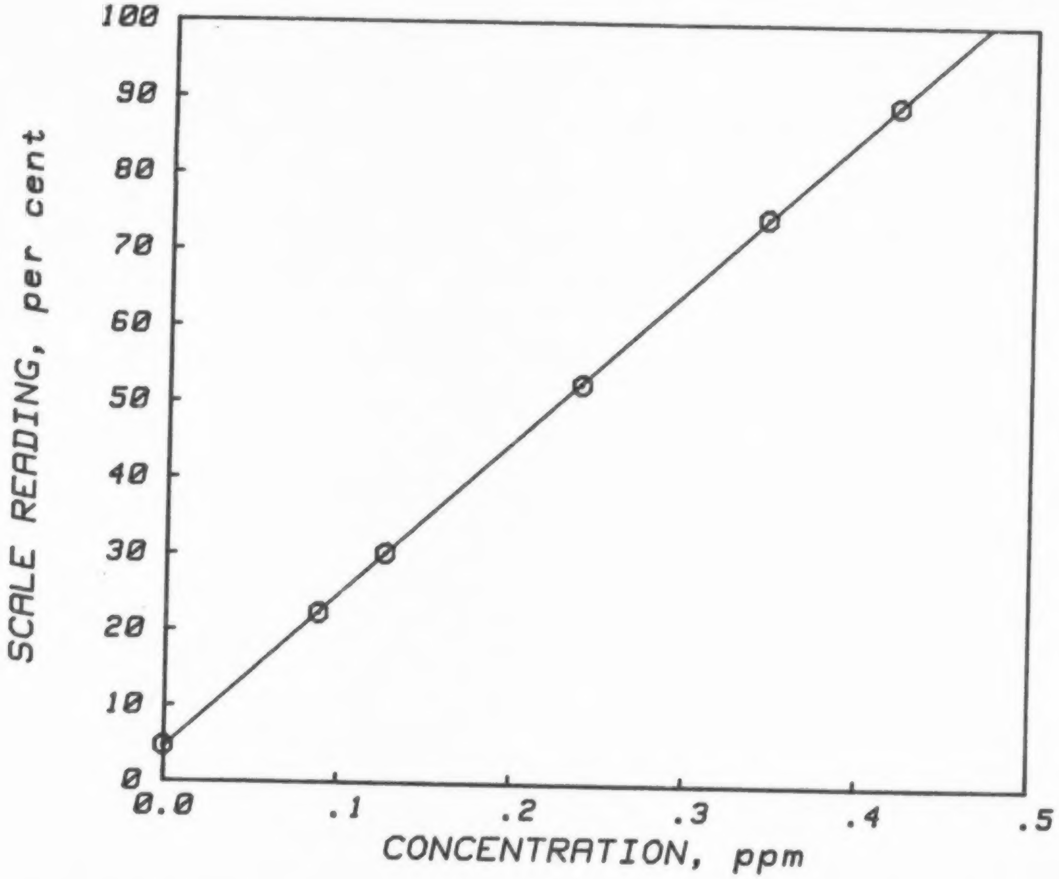
Performance parameters	Units	EPA specs.[a]	Manufacturer's test results[b]	EPA test results[c]
Noise – 0% URL	ppm	0.005	< 0.001	0.001
Noise – 80% URL	ppm	0.005	0.001	0.001
Lower detectable limits	ppm	0.01	0.010	0.009
Interferents	ppm			
Meta-xylene		±0.02	Not tested	0.009
NO_2		±0.02	−0.006	0.000
NO		±0.02	0.004	0.009
O_3		±0.02	−0.004	−0.003
Naphthalene		±0.02	0.000	< −0.001
H_2S		±0.02	Not tested	0.001
H_2O		±0.02	< −0.001	0.005
Total		≤0.06	0.015[d]	0.028[d]
Zero drift – 12 h	ppm	±0.02	0.003[d]	0.012[d]
Zero drift – 24 h	ppm	±0.02	0.002[d]	0.003[d]
Span drift – 20% URL	%	±20.0	1.77[d]	2.21[d]
Span drift – 80% URL	%	±5.0	0.52[d]	1.28[d]
Lag time	min	20	0.2	0.8
Rise time	min	15	2.9	1.8
Fall time	min	15	3.0	1.8
Precision – 20% URL	ppm	0.010	< 0.001	0.000
Precision – 80% URL	ppm	0.015	< 0.001	0.001

[a] From EPA equivalency regulations, 40 CFR Part 53.

[b] Average, from manufacturer's application for equivalency determination.

[c] Average, from EPA Phase I postdesignation tests.

[d] Average of absolute values.



```
ANALYZER:     MELOY             Y = MX + A           DATA:   X          Y
MODEL:        SA 700                                       -----      -----
SERIAL No.:   OF 106            M =   201.938          1   0.000       4.700
POLLUTANT:    SO2                95% C.I.= ± 1.512     2    .089      22.300
RANGE:         .5 ppm                                  3    .127      30.200
LOCATION:     135               A =     4.539          4    .239      52.600
DATE:         01/18/83           95% C.I.= ±  .379     5    .346      74.600
DATE CODE:     83.018                                  6    .421      89.500
NAME:         C F SMITH         r =    .99999
```

Figure 38. Typical calibration curve for the Meloy SA700.

Manufacturer's Recommended Maintenance

Operation	Frequency
Clean or replace pneumatic lines	Annually
Clean rotameter	Annually
Clean flow control valve	Annually
Repack zero air filter	Quarterly
Replace solenoid valve	Biannually
Rebuild or replace pump	Annually
Clean dryer	Annually
Replace hydrocarbon scrubber	Annually
Clean optics	Quarterly
Clean fan, air filter, chassis	Quarterly
Clean reactor	Annually

Malfunctions

May 1982	During initial setup and calibration, the intensity circuit was out of the control range and readjustment was required. After consultation with Meloy and performance of the alignment procedure, the problem was corrected.
July 1-8, 1982	Analyzer displayed excessive zero drift, approximately 2 to 3 percent/day. Meloy indicated that this was not normal performance and, at their suggestion, the analyzer was returned for warranty service.
January 26, 1983	Analyzer output was erratic. A Meloy representative replaced the UV lamp, installed a new-style lamp mount, and performed alignment and intensity circuit control adjustments to correct the problem.
March 18, 1983	Span drift test failure. The lamp intensity control circuit was out of adjustment (see General Comments).

General Comments

On March 18, 1983, the SA700 analyzer failed a span drift test due to a malfunction of the lamp intensity control circuit. Meloy representatives arrived with a new SA700 analyzer on March 24, 1983. After performing the intensity circuit control adjustment procedure and checking the analyzer for 2 days, Meloy representatives could find no cause for the malfunction. To avoid additional delay, EPA and Meloy agreed to repeat the span drift test on the new SA700 analyzer. No test failures were observed on the new analyzer. Performance of the malfunctioning analyzer's intensity control circuit later appeared to be normal and no reason for the malfunction was found.

Figure 39. Monitor Labs Model 8450 Sulfur Monitor (EQSA-0876-013). Monitor Labs, Incorporated, 10180 Scripps Ranch Boulevard, San Diego, CA 92131.

General Description

The Monitor Labs 8450 sulfur dioxide analyzer operates on the principle of flame photometric detection as described in Appendix A. It is equipped with a heated silver gauze scrubber to remove ambient hydrogen sulfide, making it unresponsive to that compound. This type of scrubber has been known to produce both positive and negative interference to the SO_2 analysis when ambient levels of ozone are present in the sample. (See description of the measurement principle in Appendix A.) These interferences, however, are minimized by passing the sample through a heated chamber upstream of the scrubber, thus destroying any ozone present before it reaches the silver gauze.

The digital electronic techniques used to produce a linear output also accept and process negative data. This capability prevents the possibility of nonapparent negative zero offset in the linearization process.

The analyzer is packaged in two separate modules. One contains the signal-processing electronics and the other contains the detector and the sample-handling pneumatics. To be used as an equivalent analyzer, the Model 8450 must be operated on a range of either 0 to 0.5 or 0 to 1.0 ppm, with a 5-second time constant, with a Model 8740 hydrogen sulfide scrubber in the sample line, and with or without any of the following options:

BP	Bipolar signal processor
V	Zero/span valves
VT	Zero/span valves and timer
TF	TFE sample particulate filter
IZS	Internal zero/span module
CLO	Current loop output
DO	Status remote interface.

Ambient air surrounding the analyzer must be within the range of 20° to 30° C, inclusive, and line voltage for the analyzer must be within 105 to 125 Vac, inclusive.

TABLE 11. MONITOR LABS 8450 LABORATORY PERFORMANCE TEST RESULTS

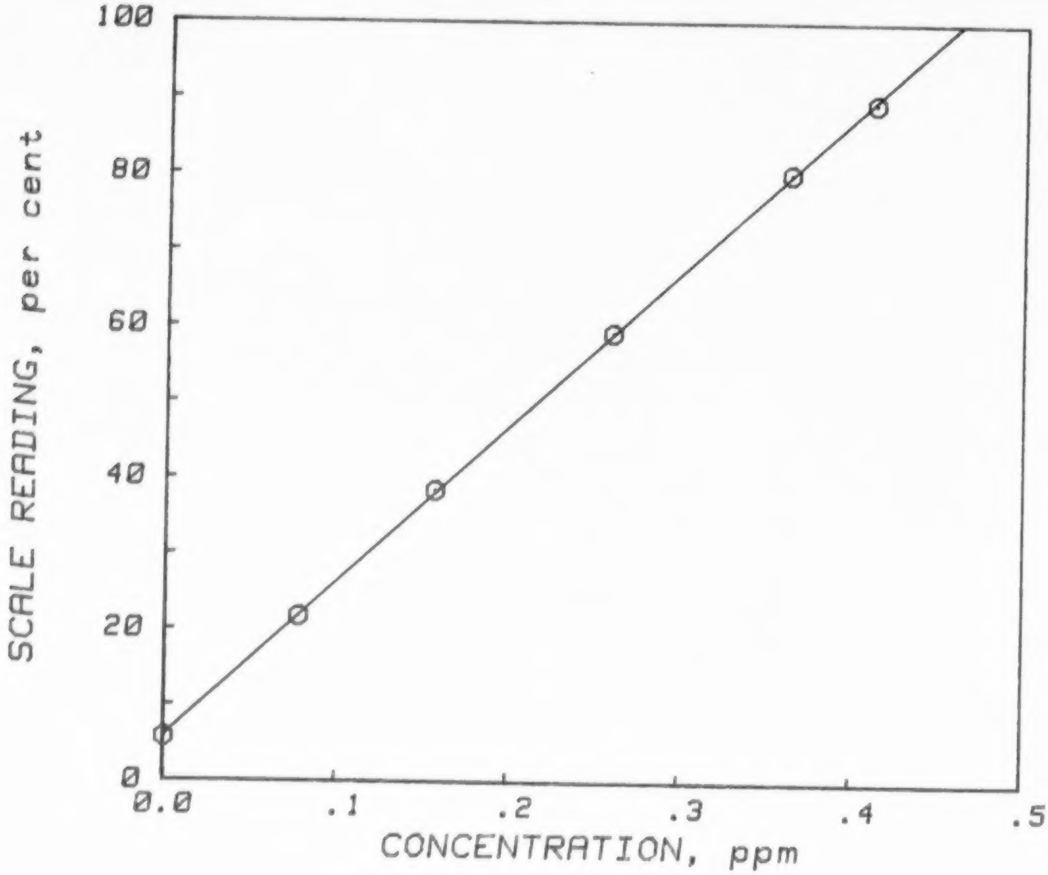
Performance parameters	Units	EPA specs.[a]	Manufacturer's test results[b]	EPA test results[c]
Noise — 0% URL	ppm	0.005	0.001	<0.001
Noise — 80% URL	ppm	0.005	0.001	0.001
Lower detectable limits	ppm	0.01	0.013	0.009
Interferents	ppm			
CO		±0.02	< −0.001	−0.002
H_2O		±0.02	−0.012	−0.003
CO_2		±0.02	−0.018	−0.019
H_2S		±0.02	0.001	0.017
O_3		±0.02	0.004	−0.007
Total		≤0.06	0.035[d]	0.048[d]
Zero drift — 12 h	ppm	±0.02	0.001[d]	0.001[d]
Zero drift — 24 h	ppm	±0.02	0.001[d]	0.004[d]
Span drift — 20% URL	%	±20.0	1.06[d]	1.49[d]
Span drift — 80% URL	%	±5.0	0.85[d]	1.00[d]
Lag time	min	20	<1	0.3
Rise time	min	15	<1	1.6
Fall time	min	15	<1	2.1
Precision — 20% URL	ppm	0.010	0.001	0.002
Precision — 80% URL	ppm	0.015	0.001	0.002

[a] From EPA equivalency regulations, 40 CFR Part 53.

[b] Average, from manufacturer's application for equivalency determination.

[c] Average, from EPA Phase I postdesignation tests, Serial Number 147.

[d] Average of absolute values.



ANALYZER: MONITOR LABS
MODEL: 8450
SERIAL No.: 147
POLLUTANT: SO2
RANGE: .5 ppm
LOCATION: DAMDF
DATE: 03/30/79
DATE CODE: 79.089
NAME: PHASE II

Y = MX + A

M = 203.674
95% C.I.= ± 2.764

A = 5.939
95% C.I.= ± .713

r = .99995

DATA:	X	Y
1	0.000	5.700
2	.078	21.700
3	.157	38.300
4	.260	59.100
5	.363	80.100
6	.412	89.400

Figure 40. Typical calibration curve for the Monitor Labs 8450.

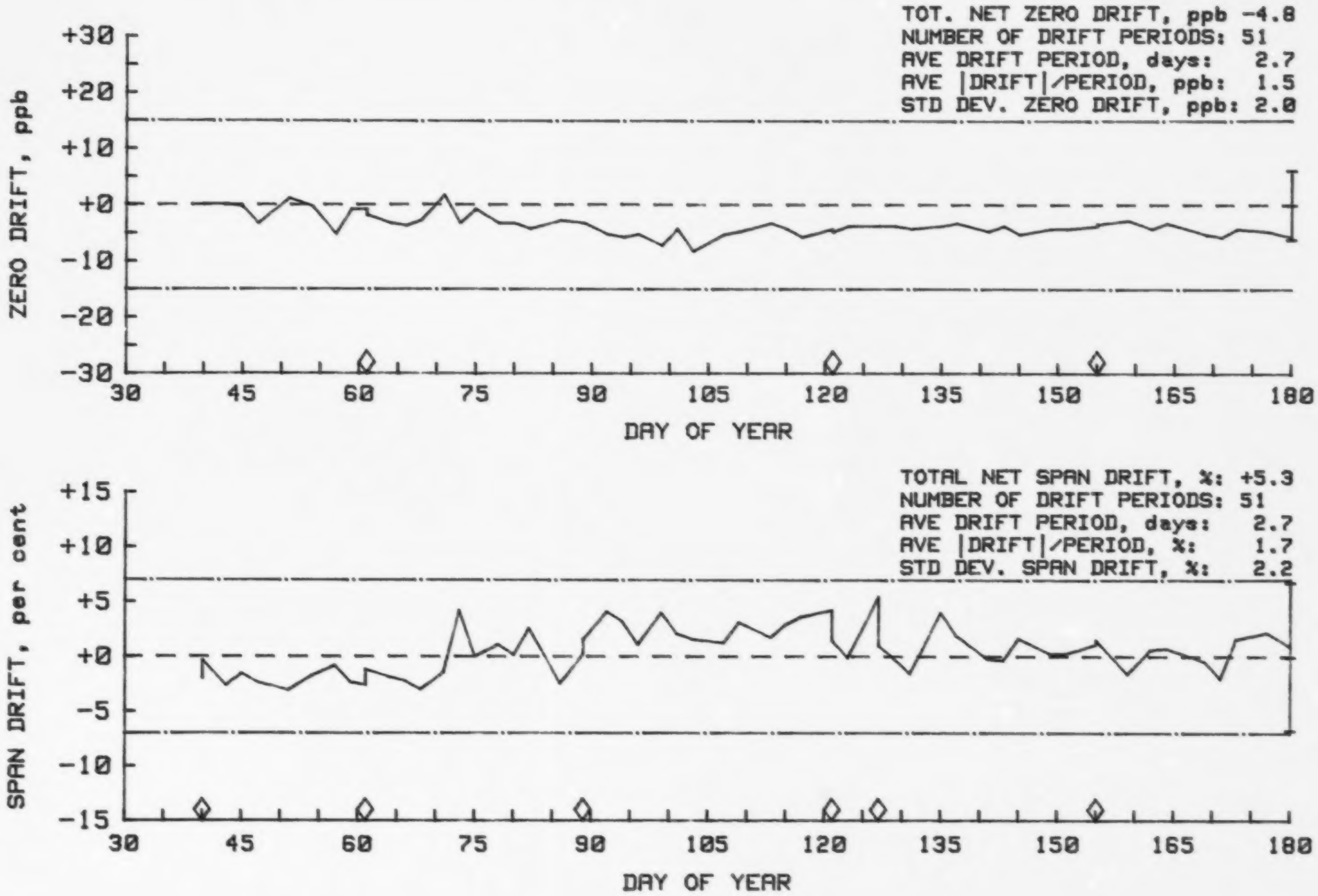


Figure 41. Zero and span drift in the Monitor Labs 8450 SO_2 readings during the Phase II ambient monitoring test.

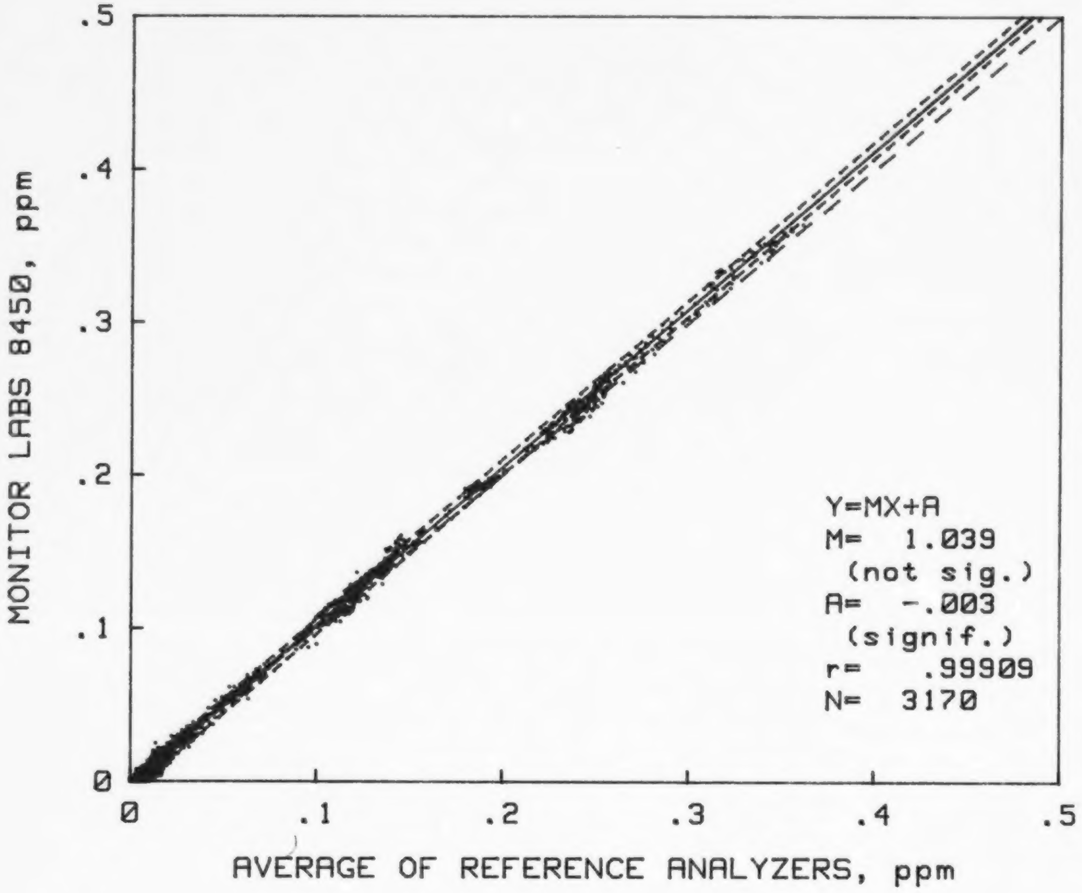
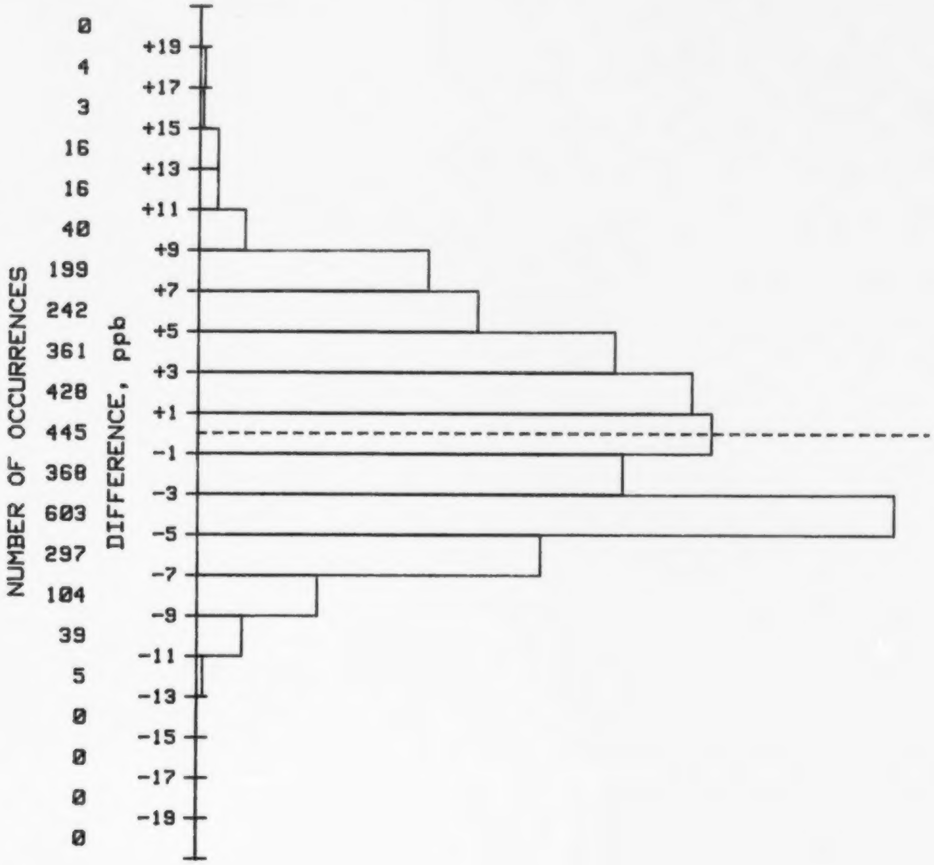
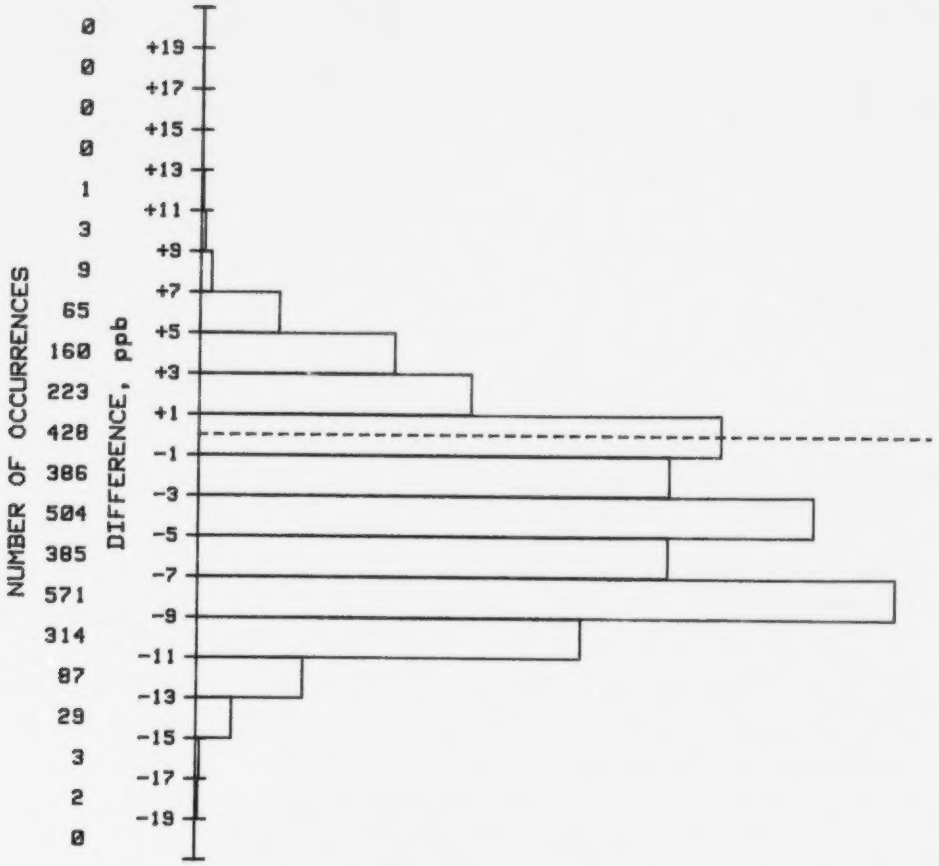


Figure 42. Relationship between the Monitor Labs 8450 and the average of the other analyzers during the Phase II ambient monitoring test.



TOTAL No. OF DATA PAIRS: 3170
CORRELATION COEFFICIENT: .999087
MEAN DIFFERENCE, ppb: +.02
STD. DEVIATION OF DIFFERENCES, ppb: 4.7655
MAX. ABSOLUTE DIFFERENCE, ppb: 19
NO. ABSOLUTE DIFFERENCES >20: 0

Figure 43. Frequency distribution of differences in hourly SO_2 ambient air readings between the Monitor Labs 8450 and the average of simultaneous readings from the other analyzers during the Phase II ambient monitoring test. All readings corrected for zero and span drift.



```
TOTAL No. OF DATA PAIRS:                 3170
CORRELATION COEFFICIENT:                      .998799
MEAN DIFFERENCE, ppb:                     -4.01
STD. DEVIATION OF DIFFERENCES, ppb:        4.5471
MAX. ABSOLUTE DIFFERENCE, ppb:            18
NO. ABSOLUTE DIFFERENCES >20:              0
```

Figure 44. Frequency distribution of differences in hourly SO_2 ambient air readings between the Monitor Labs 8450 and the average of simultaneous readings from the other analyzers during the Phase II ambient monitoring test. Monitor Labs 8450 readings are not corrected for zero and span drift.

Manufacturer's Recommended Maintenance

Operation	Frequency
Examine rotameter assembly.	Weekly
Examine exhaust lines.	Weekly
Check vacuum.	Weekly
Examine, clean, or replace fan filter.	Every 15-30 days
Check or replace chopper drive belt.	Every 30 days
Replace sample filter.	Every 30 days
Check H_2 regulator.	Every 150 days
Check exhaust orifice and filter.	Every 150 days
Replace zero/span charcoal filter.	Every 300 days
Replace H_2S scrubber.	Every 300 days
Examine or clean window.	Every 300 days
Examine or clean purge air filter.	Every 300 days
Examine or clean zero/span air filter.	Every 300 days

Various other maintenance operations are specified on an "as required" basis.

Malfunctions

February 1977 (initial startup)	Linearizer card replaced. Power supply card replaced.
During Phase I testing	Failed initial ozone and and hydrogen sulfide interferent tests (see General Comments).
1-17-79	Chopper motor was replaced.

General Comments

During Phase I testing, the analyzer failed initial ozone and hydrogen sulfide interferent tests. Additionally, performance during the CO_2 interferent test was marginal. According to the manufacturer's recommendation, the H_2S scrubber pads were replaced but with no improvement in test performance. The manufacturer then changed the formulation of the scrubber pads from plated to pure silver pads. With the new, pure silver pads installed, the analyzer passed the ozone and H_2S interferent tests. The manufacturer supplied the reformulated scrubber pads to all analyzer owners who were originally supplied with the old pads. The CO_2 interference, however, remained marginal.

During 215 days of Phase II testing, data were lost for 17 days because of malfunctions.

Phase II Testing Operator's Comments

The analyzer required 30 to 45 min to come to equilibrium on span gas, which lengthened the time required for routine zero/span operations.

The electrical and optical test modes featured in this analyzer serve as convenient quality control checks on day-to-day condition of the instrument.

The LED display is more convenient to read than a conventional meter display.

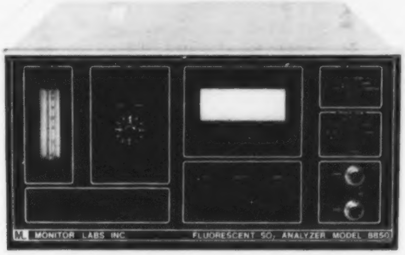


Figure 45. Monitor Labs Model 8850 Fluorescent SO_2 Analyzer (EQSA-0779-039). Monitor Labs, Incorporated, 10180 Scripps Ranch Boulevard, San Diego, CA 92131.

General Description

The Monitor Labs 8850 sulfur dioxide analyzer operates on the principle of fluorescence as described in Appendix A. It uses mechanically chopped ultraviolet excitation radiation to provide signal modulation for amplification. The analyzer is equipped with an unheated scrubber to remove aromatic hydrocarbons that would otherwise produce a positive interference with the fluorescence technique. Removal of ambient moisture is not required because judicious selection of the excitation wavelength minimizes the effect of this potential interferent.

To be used as an equivalent analyzer, the Model 8850 must be operated on a range of either 0 to 0.5 or 0 to 1.0 ppm, with an internal time constant setting of 55 seconds, with a TFE sample filter installed on the sample inlet line, and with or without any of the following options:

• 03A	Rack
• 03B	Slides
• 05A	Valves zero/span
• 06A	IZS, internal zero/span source
• 06B,C,D	NBS-traceable permeation tubes
• 08A	Pump
• 09A	Rack mount for option 08A
• 010	Status output w/connector
• 013	Recorder output options
• 014	DAS output options
• 017	Low flow option.

Ambient air surrounding the analyzer must be within the range of 20° to 30° C, inclusive, and line voltage to the analyzer must be within the range of 105 to 125 Vac, inclusive.

TABLE 12. MONITOR LABS 8850 LABORATORY PERFORMANCE TEST RESULTS

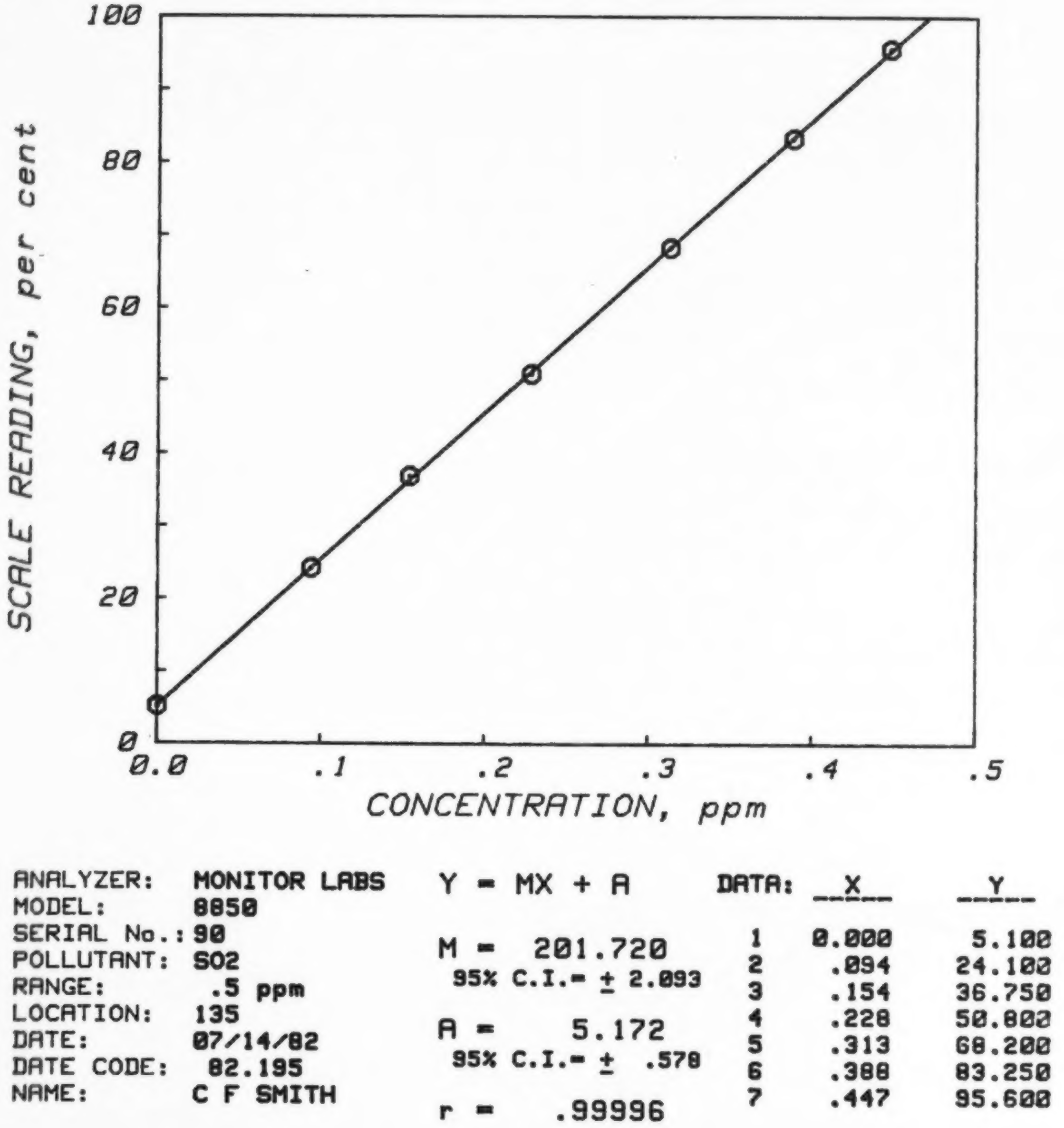
Performance parameters	Units	EPA specs.[a]	Manufacturer's test results[b]	EPA test results[c]
Noise — 0% URL	ppm	0.005	<0.001	<0.001
Noise — 80% URL	ppm	0.005	0.001	0.001
Lower detectable limits	ppm	0.01	0.019	0.010
Interferents	ppm			
H_2O		±0.02	0.003	0.007
NO		±0.02	0.003	0.005
NO_2		±0.02	0.001	0.002
O_3		±0.02	−0.004	−0.004
Naphthalene		±0.02	< −0.001	0.001
Meta-xylene		±0.02	Not tested	0.002
H_2S		±0.02	Not tested	0.000
Total		≤0.06	0.011[d]	0.021[d]
Zero drift — 12 h	ppm	±0.02[d]	0.001[d]	0.002[d]
Zero drift — 24 h	ppm	±0.02	0.001[d]	0.005[d]
Span drift — 20% URL	%	±20.0	1.38[d]	3.46[d]
Span drift — 80% URL	%	±5.0	1.41[d]	0.56[d]
Lag time	min	20	0.3	0.5
Rise time	min	15	3.8	3.9
Fall time	min	15	3.8	3.9
Precision — 20% URL	ppm	0.010	0.001	<0.001
Precision — 80% URL	ppm	0.015	0.002	0.001

[a] From EPA equivalency regulations, 40 CFR Part 53.

[b] Average, from manufacturer's application for equivalency determination.

[c] Average, from EPA Phase I postdesignation tests.

[d] Average of absolute values.



```
ANALYZER:    MONITOR LABS    Y = MX + A       DATA:   X        Y
MODEL:       8850                                    -----    -----
SERIAL No.:  90                                 1    0.000     5.100
POLLUTANT:   SO2             M =   201.720      2     .094    24.100
RANGE:        .5 ppm          95% C.I.= ± 2.093 3     .154    36.750
LOCATION:    135                                4     .228    50.800
DATE:        07/14/82        A =      5.172     5     .313    68.200
DATE CODE:    82.195          95% C.I.= ±  .578 6     .388    83.250
NAME:        C F SMITH                          7     .447    95.600
                             r =    .99996
```

Figure 46. Typical calibration curve for the Monitor Labs 8850.

Manufacturer's Recommended Maintenance

Operation	Frequency
Recharge or replace zero/span module charcoal filter	Every 90 days
Replace gas sample particulate filter	Every 30 days
Examine rotameter assembly	Weekly
Examine exhaust lines and vacuum	Weekly
Examine exhaust orifice	Every 180 days
Examine exhaust orifice filter	Every 180 days
Examine fan filter	Every 15-30 days
Examine zero/span air filter	Annually
Examine UV lamp	Every 30 days
Replace UV lamp	Annually
Replace catalyst	Annually

Various other maintenance operations are specified on an "as-required" basis.

Malfunctions

October 13, 1982[*]	Span drift test failure (see General Comments).
October 29, 1982[†]	Span drift test failure (see General Comments).
May 24, 1983[‡]	Span drift test failure (see General Comments).

General Comments

On October 13, 1982, the analyzer (SN 90) failed a span drift test. The cause of the failure was not apparent. The analyzer was originally purchased in March 1980 and was operated continuously from September 23, 1980, until the end of June 1982. A second (new) 8850 analyzer (SN 717) was tested for span drift to determine whether the span drift failure was caused by prolonged use (approximately 2 years) of the analyzer prior to the tests or whether it was typical of the performance of the analyzer.

On October 29, 1982, the new 8850 analyzer (SN 717) also failed a span drift test. Monitor Labs was immediately contacted concerning the test failures. After conducting some abbreviated span drift tests on 10 current production analyzers, Monitor Labs observed the same performance deficiency on approximately half of the tested analyzers. The performance deficiency was attributed to the PMT thermostatic control circuits. The performance deficiency has been corrected with a simple modification of the mixer circuit board assembly. To maintain the designation status of the Model 8850 analyzers sold prior to implementation of this modification, Monitor Labs has supplied the ultimate purchasers of those previously sold analyzers with an update kit to implement the modification.

---

[*] Monitor Labs 8850 SN 90.

[†] Monitor Labs 8850 SN 717.

[‡] Monitor Labs 8850 SN 90, modified as per Monitor Labs change drawing #885-0833 and #885-0834.

On May 24, 1983, a modified 8850 analyzer (SN 90) again failed a span drift test. This failure was attributed to a malfunction of the PMT thermoelectric cooler. Subsequent to replacement of the thermoelectric cooler, the modified analyzer successfully passed the repeated span drift tests.

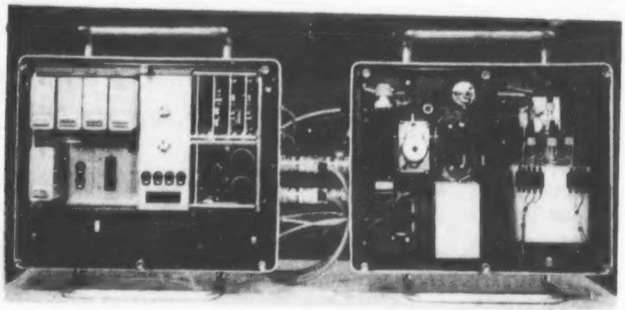


Figure 47. Philips PW9700 SO_2 Analyzer (EQSA-0876-011).
Philips Electronic Instruments, Inc.,
85 McKee Drive, Mahwah, NJ 07430.

General Description

The Philips Model PW9700 sulfur dioxide analyzer operates on the principle of coulometric detection as described in Appendix A. It is equipped with a heated chemical scrubber that removes species interfering with the coulometric detection of SO_2 (e.g., oxidizing or reducing species), thus making it essentially specific for SO_2. The analyzer is supplied in two separate modules--one containing the power supply and the vacuum pump and the other containing the detector, sample handling pneumatics, and electronics.

This model has been superseded by the Philips Model PW9755, but its designation is still maintained. To be used as an equivalent analyzer, the model PW9700 must be operated on the 0-to-0.5-ppm range and with a reference voltage of 760 mV. Ambient air surrounding the analyzer must be within the range of 20° to 30° C, inclusive, and line voltage to the analyzer must be within the range of 105 to 125 Vac, inclusive.

TABLE 13. PHILIPS PW9700 LABORATORY PERFORMANCE TEST RESULTS

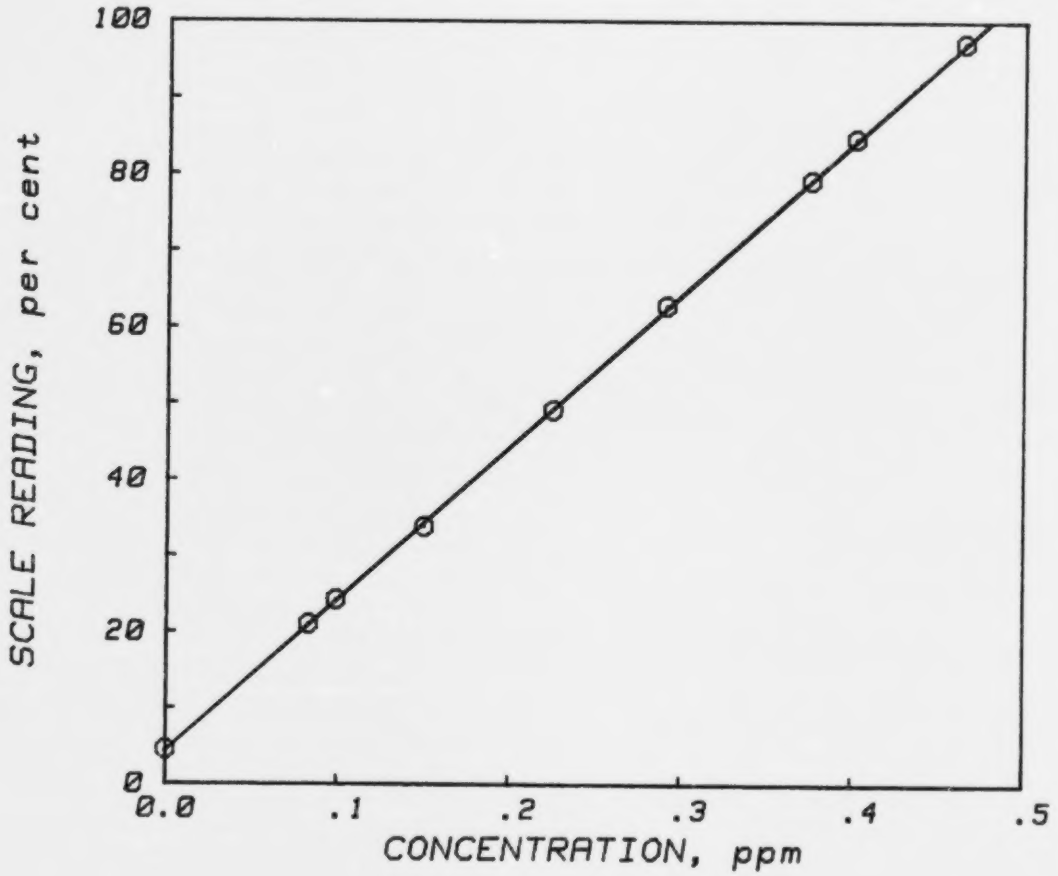
Performance parameters	Units	EPA specs.[a]	Manufacturer's test results[b]	EPA test results[c]
Noise — 0% URL	ppm	0.005	<0.001	0.000
Noise — 80% URL	ppm	0.005	0.001	0.001
Lower detectable limits	ppm	0.01	0.009	0.007
Interferents	ppm			
O_3		±0.02	0.008	−0.008
NO		±0.02	0.000	0.001
NO_2		±0.02	0.004	−0.001
H_2S		±0.02	0.001	<0.001
C_2H_2		±0.02	0.000	−0.001
H_2O		±0.02	0.000	0.009
NH_3		±0.02	0.000	0.000
HCl		±0.02	<0.001	−0.001
Total		≤ 0.06	0.013[d]	0.021[d]
Zero drift — 12 h	ppm	±0.02	<0.001[d]	0.001[d]
Zero drift — 24 h	ppm	±0.02	0.002[d]	0.002[d]
Span drift — 20% URL	%	±20.0	3.00[d]	5.0[d]
Span drift — 80% URL	%	±5.0	1.01[d]	1.8[d]
Lag time	min	20	0.8	0.2
Rise time	min	15	3.5	2.2
Fall time	min	15	3.8	1.4
Precision — 20% URL	ppm	0.010	<0.001	0.001
Precision — 80% URL	ppm	0.015	0.000	0.002

[a] From EPA equivalency regulations, 40 CFR Part 53.

[b] Average, from manufacturer's application for equivalency determination.

[c] Average, from EPA Phase I postdesignation tests.

[d] Average of absolute values.



ANALYZER: PHILIPS
MODEL: PW 9700
SERIAL No.: D1415C
POLLUTANT: SO2
RANGE: .5 ppm
LOCATION: RTI
DATE: 05/16/78
DATE CODE: 78.136
NAME: PHASE I

$Y = MX + A$

$M = 200.136$
95% C.I. = ± 1.378

$A = 4.291$
95% C.I. = ± .382

$r = .99997$

DATA:	X	Y
1	0.000	4.500
2	.083	21.000
3	.099	24.200
4	.150	33.800
5	.225	49.100
6	.291	62.800
7	.375	79.200
8	.401	84.700
9	.464	97.200

Figure 48. Typical calibration curve for the Philips PW9700.

Manufacturer's Recommended Maintenance

Operation	Frequency
Replace glass fiber membrane in sampler unit	Every 3 months
Flush vacuum pump	Every 3 months
Replace silver gauge of the selectivity filter	Every 3 months
Replace glass fiber membrane of aerosol filter	Every 3 months
Replace measuring solution	Every 3 months
Calibrate SO_2 source	Every 3 months

Malfunctions

September 22, 1978	Failure of reference electrode

General Comments

Only Phase I testing has been performed; Phase II testing is not anticipated as this analyzer has been superseded by the Philips PW 9750.

During 153 days of Phase I testing, data were lost for 23 days due to malfunctions.

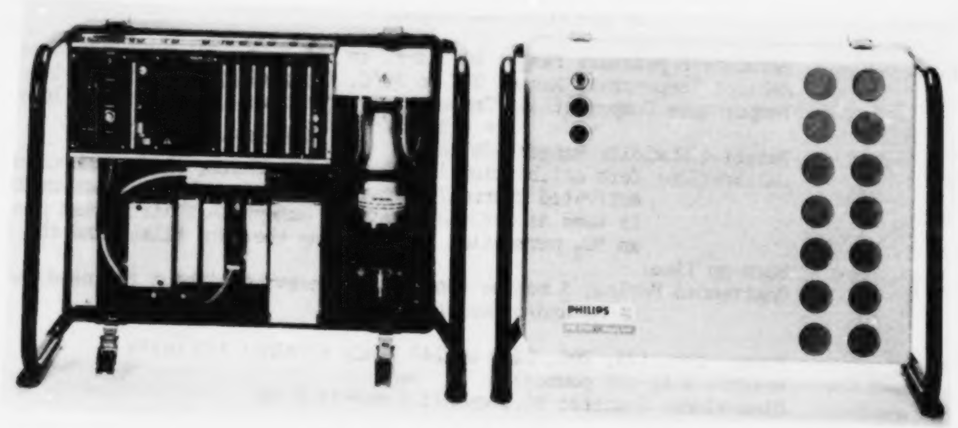


Figure 49. Philips PW9755 Sulfur Dioxide Analyzer (EQSA-0676-010). Philips Electronic Instruments, Inc., 85 McKee Drive, Mahwah, NJ 07430.

General Description

The Philips Model PW9755 sulfur dioxide analyzer operates on the principle of coulometric detection as described in Appendix A. It is equipped with a heated, chemical scrubber, which removes species interfering with the coulometric detection of SO_2 (e.g., oxidizing or reducing species), thus making it essentially specific for SO_2. The analyzer is packaged in two separate modules--one containing the power supply and vacuum pump and the other containing the detector, sample-handling pneumatics, and electronics. The power supply module can be equipped to power three Philips instruments simultaneously.

To be used as an equivalent analyzer, the Model PW9755 must be operated on the 0-to-0.5-ppm range and with a reference voltage setting of 760 mV, with or without any of the following options:

- PW9752/00 Air sampler manifold
- PW9753/00 Mounting rack for accessories
- PW9750/30 Frame for MTT
- PW9750/41 Control clock 60 Hz
- PW9754/00 Air distributor.

Ambient air surrounding the analyzer must be within the range of 20° to 30° C, inclusive, and line voltage to the analyzer must be within the range of 105 to 125 Vac, inclusive.

TABLE 14. PHILIPS PW9755 LABORATORY PERFORMANCE TEST DATA

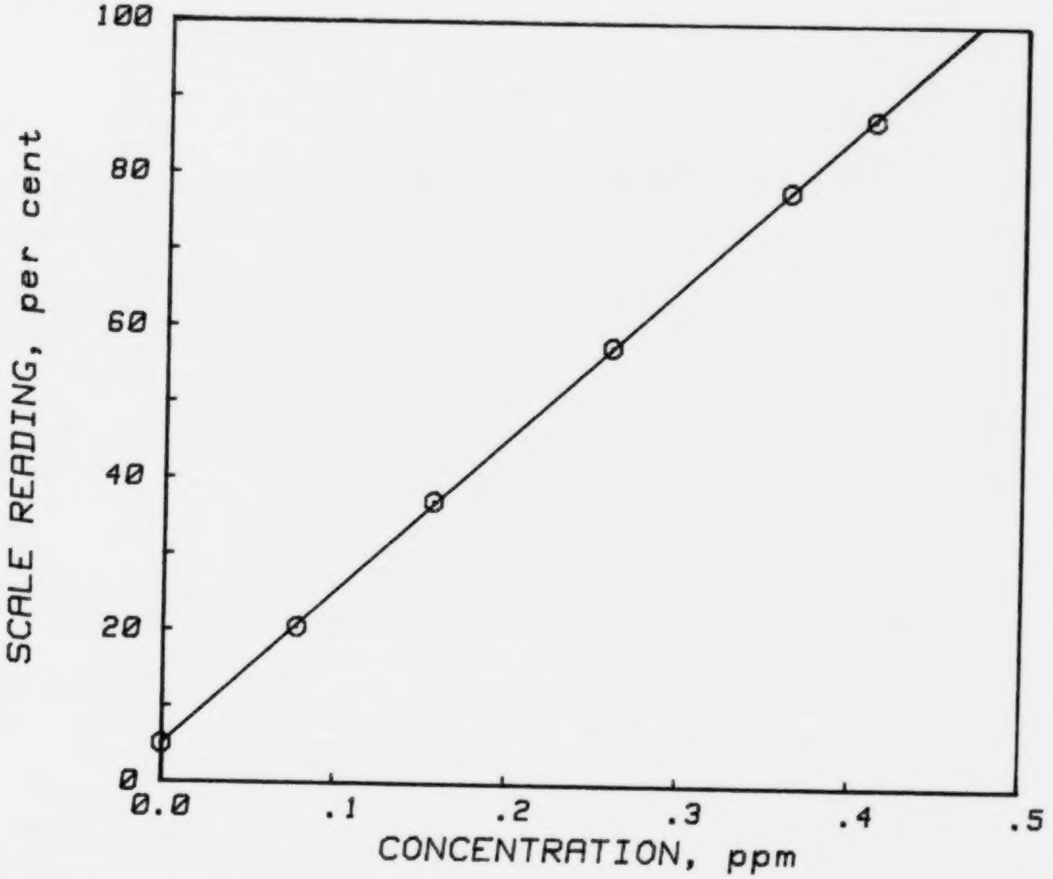
Performance parameters	Units	EPA specs.[a]	Manufacturer's test results[b]	EPA test results[c]
Noise – 0% URL	ppm	0.005	< 0.001	0.000
Noise – 80% URL	ppm	0.005	0.003	0.002
Lower detectable limit	ppm	0.01	0.009	0.009
Interferents	ppm			
NO		±0.02	0.000	0.000
O_3		±0.02	0.008	− 0.004
NO_2		±0.02	0.004	0.000
H_2S		±0.02	0.001	0.000
H_2O		±0.02	0.000	0.002
HCl		±0.02	< 0.001	0.000
C_2H_4		±0.02	0.000	< 0.001
NH_3		±0.02	0.000	< 0.001
Total		< 0.06	0.013[d]	0.006[d]
Zero drift – 12 h	ppm	±0.02	0.001[d]	0.002[d]
Zero drift – 24 h	ppm	±0.02	0.001[d]	0.003[d]
Span drift – 20% URL	%	±20.0	1.27[d]	1.35[d]
Span drift – 80% URL	%	±5.0	0.61[d]	0.3[d]
Lag time	min	20	0.6	0.6
Rise time	min	15	2.6	0.7
Fall time	min	15	2.7	0.8
Precision – 20% URL	ppm	0.010	< 0.001	< 0.001
Precision – 80% URL	ppm	0.015	< 0.001	0.001

[a] From EPA equivalency regulations, 40 CFR Part 53.

[b] Average, from manufacturer's application for equivalency determination.

[c] Average, from EPA Phase I postdesignation tests.

[d] Average absolute values.



```
ANALYZER:    PHILIPS          Y = MX + A          DATA:   X          Y
MODEL:       PW 9755                                    -----      -----
SERIAL No.:  612              M =   200.753          1  0.000      5.000
POLLUTANT:   SO2               95% C.I.= ± 2.482     2   .078     20.400
RANGE:         .5 ppm                                3   .157     37.000
LOCATION:    DAMDF            A =      5.074         4   .260     57.500
DATE:        03/30/79          95% C.I.= ±  .641     5   .363     78.000
DATE CODE:    79.089                                 6   .412     87.500
NAME:        PHASE II         r =    .99996
```

Figure 50. Typical calibration curve for the Philips PW9755.

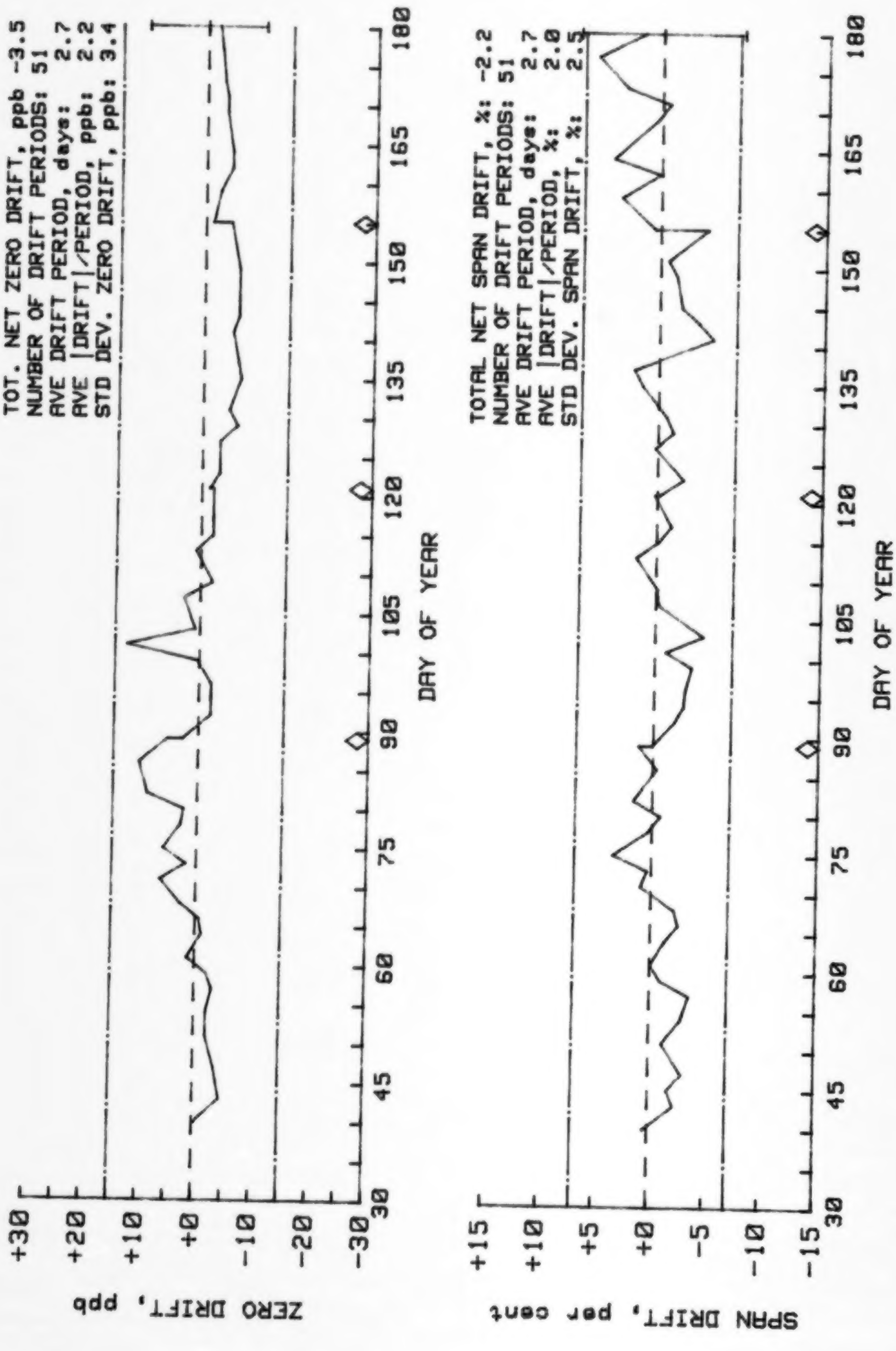


Figure 51. Zero and span drift in the Philips PW9755 SO_2 readings during the Phase II ambient monitoring test.

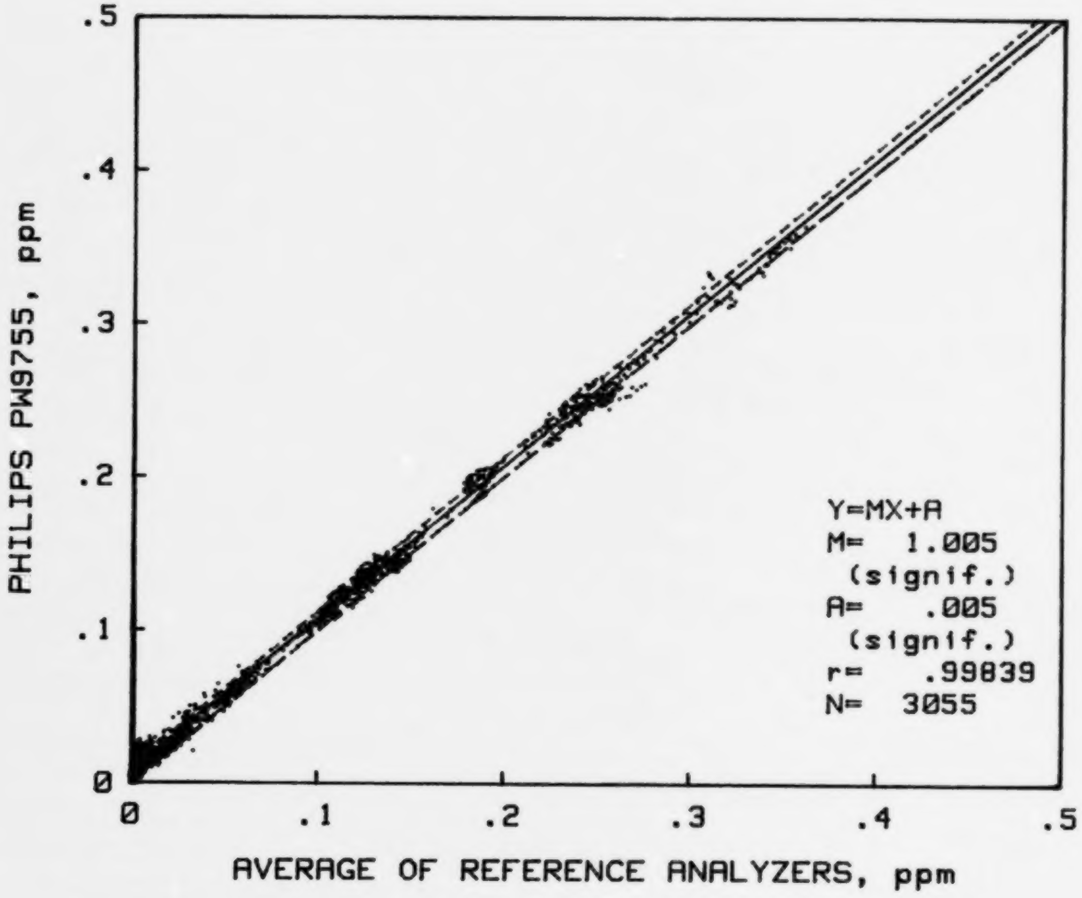
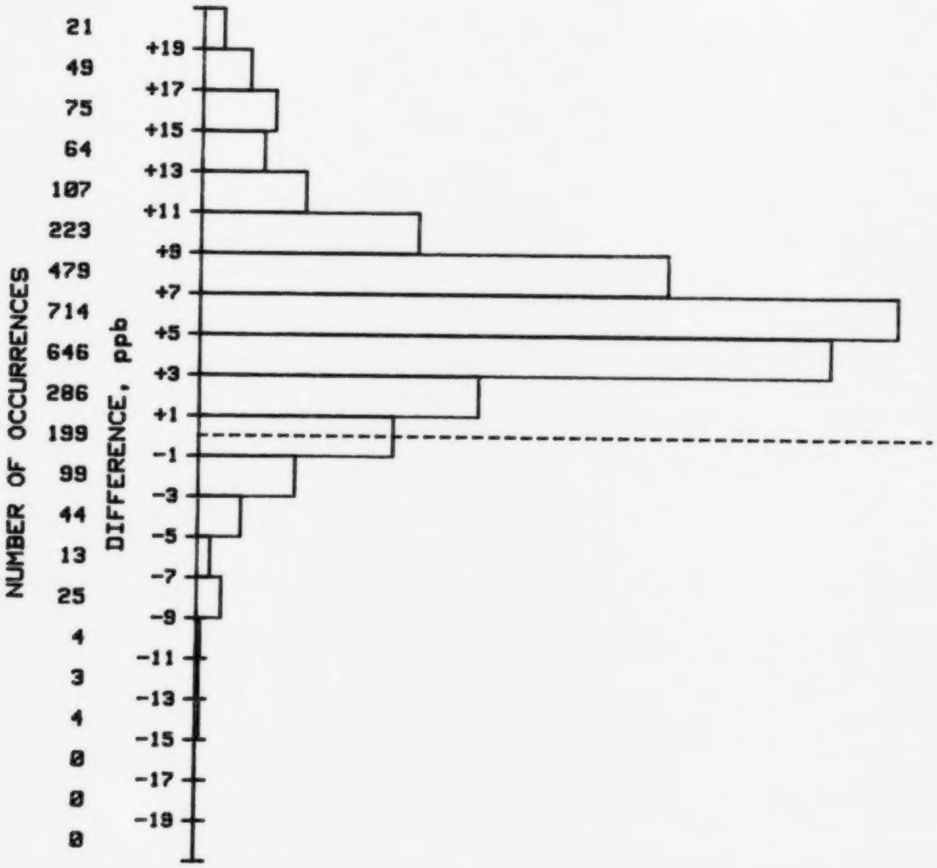
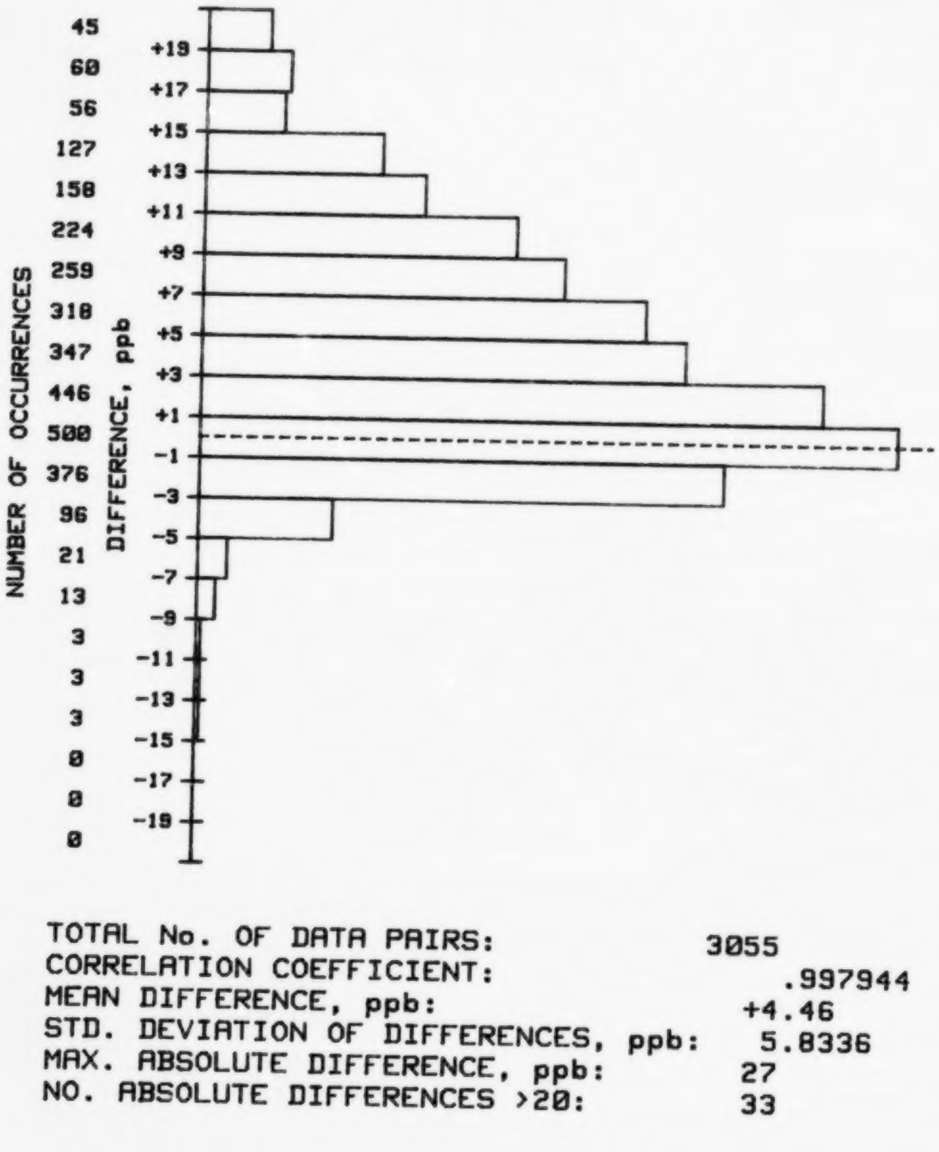


Figure 52. Relationship between the Philips PW9755 and the average of the other analyzers during the Phase II ambient monitoring test.



```
TOTAL No. OF DATA PAIRS:                3055
CORRELATION COEFFICIENT:                    .998388
MEAN DIFFERENCE, ppb:                    +5.68
STD. DEVIATION OF DIFFERENCES, ppb:       4.6768
MAX. ABSOLUTE DIFFERENCE, ppb:           25
NO. ABSOLUTE DIFFERENCES >20:            15
```

Figure 53. Frequency distribution of differences in hourly SO_2 ambient air readings between the Philips PW9755 and the average of simultaneous readings from the other analyzers during the Phase II ambient monitoring test. All readings corrected for zero and span drift.



```
TOTAL No. OF DATA PAIRS:                    3055
CORRELATION COEFFICIENT:                        .997944
MEAN DIFFERENCE, ppb:                         +4.46
STD. DEVIATION OF DIFFERENCES, ppb:            5.8336
MAX. ABSOLUTE DIFFERENCE, ppb:                27
NO. ABSOLUTE DIFFERENCES >20:                 33
```

Figure 54. Frequency distribution of differences in hourly SO_2 ambient air readings between the Philips PW9755 and the average of simultaneous readings from the other analyzers during the Phase II ambient monitoring test. Philips PW9755 readings are <u>not corrected for zero and span drift</u>.

Manufacturer's Recommended Maintenance

Operation	Frequency
Replace sample filter.	Monthly
Replace scrubber cartridge.	Every 3 mo
Check electrolyte level.	Every 3 mo
Measure flow through detector.	Every 3 mo
Measure total flow.	Every 3 mo
Replace pump diaphragms.	Every 3 mo
Check pump vacuum.	Every 3 mo
Replace electrolyte.	Every 6 mo
Clean metering orifice.	Every 6 mo
Replace metering orifice filter materials.	Every 6 mo
Clean pump silencer.	Every 6 mo
Clean Peltier element.	Annually
Check pump bearings.	Annually
Replace pump crank.	Annually
Clean flushing orifice.	Every 24 mo
Replace flushing orifice filter materials.	Every 24 mo
Repack zero air filter.	Every 24 mo

Malfunctions

None.

General Comments

During Phase II testing, the flow rate through the detector dropped continuously from 145 cm^3/min (-3.3 percent) on 2-1-79 to 135 cm^3/min (-10 percent) on 6-4-79. The flow specification for the metering orifice is 150 cm^3/min (±3 percent) and is defined at conditions of 1 atm and 20° C. Ultrasonic cleaning of the orifice improved the flow rate only marginally. According to factory service personnel, this flow degradation results from corrosion of the orifice by the Br_2/Br^- measuring solution. Orifices can be purchased with bore inserts that are manufactured from a material that is less susceptible to this corrosion (e.g., sapphire).

This instrument features no provision for adjusting the zero response level. The zero voltage is always some small, upscale value (specification <10 mV) that depends on the purity and age of the electrolyte. During Phase II testing, it was noted that a span adjustment also produced a proportional change in the zero response. This change results because the span adjustment is, in reality, an amplifier or amplified gain adjustment. Because the zero baseline is always some finite voltage greater than zero, any change in the span adjustment (amplification factor) will cause a corresponding change in the zero response.

During 172 days of Phase II testing, data were lost for 0 days because of malfunctions.

Phase II Testing Operator's Comments

This instrument achieved equilibrium on span gases in less than 5 minutes.

Although the instrument manual was complicated--containing great detail on all subsystems and options--the individual sections were well written and easy to follow.

Throughout the Phase I and II testing periods this instrument required only routine preventive maintenance.

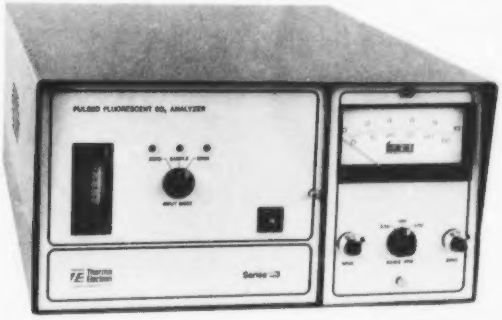


Figure 55. Thermo Electron Model 43 Pulsed Fluorescent SO_2 Analyzer (EQSA-0276-009). Thermo Electron Corporation, Environmental Instruments Division, 108 South Street, Hopkinton, MA 01748.

General Description

The Thermo Electron Model 43 sulfur dioxide analyzer operates on the principle of fluorescence as described in Appendix A. It uses pulsed ultraviolet radiation. Water vapor, which can be an interferent in this technique, is removed from the sample stream by a permeation dryer.

The analyzer is equipped with an unheated chemical scrubber called a "cutter." The cutter removes aromatic hydrocarbons (e.g., naphthalene) that would otherwise produce a positive interference in the fluorescence technique.

To be used as an equivalent analyzer, the Model 43 must be operated on a 0-to-0.5- or 0-to-1.0-ppm range, with or without any of the following options:

- 001 Rack mounting for standard 19-inch relay rack
- 002 Automatic actuation of zero and span solenoid valves
- 003 Type S flash lamp power supply
- 004 Low flow.

Ambient air surrounding the analyzer must be within the range of 20° to 30° C, inclusive, and line voltage must be within the range of 105 to 125 Vac, inclusive.

TABLE 15. THERMO ELECTRON 43 LABORATORY PERFORMANCE TEST RESULTS

Performance parameters	Units	EPA specs.[a]	Manufacturer's test results[b]	EPA test results[c]
Noise — 0% URL	ppm	0.005	0.001	0.001
Noise — 80% URL	ppm	0.005	0.001	0.002
Lower detectable limits	ppm	0.01	0.003[d]	0.009
Interferents	ppm			
Meta-xylene		±0.02	0.000	< −0.001
NO_2		±0.02	0.000	< 0.001
NO		±0.02	0.003	0.003
O_3		±0.02	−0.001	−0.002
H_2S		±0.02	0.000	Not tested
CO_2		±0.02	0.000	Not tested
CO		±0.02	−0.001	Not tested
Naphthalene		±0.02	—[e]	—[e]
Total		≤0.06	0.005[f]	0.005[f]
Zero drift — 12 h	ppm	±0.02[f]	0.005[f]	0.004[f]
Zero drift — 24 h	ppm	±0.02	0.001[f]	0.003[f]
Span drift — 20% URL	%	±20.0	0.52[f]	2.22[f]
Span drift — 80% URL	%	±5.0	0.46[f]	1.82[f]
Lag time	min	20	0.2	0.5
Rise time	min	15	3.9	4.9
Fall time	min	15	4.7	5.3
Precision — 20% URL	ppm	0.010	0.001	0.001
Precision — 80% URL	ppm	0.015	0.001	0.001

[a] From EPA equivalency regulations, 40 CFR Part 53.

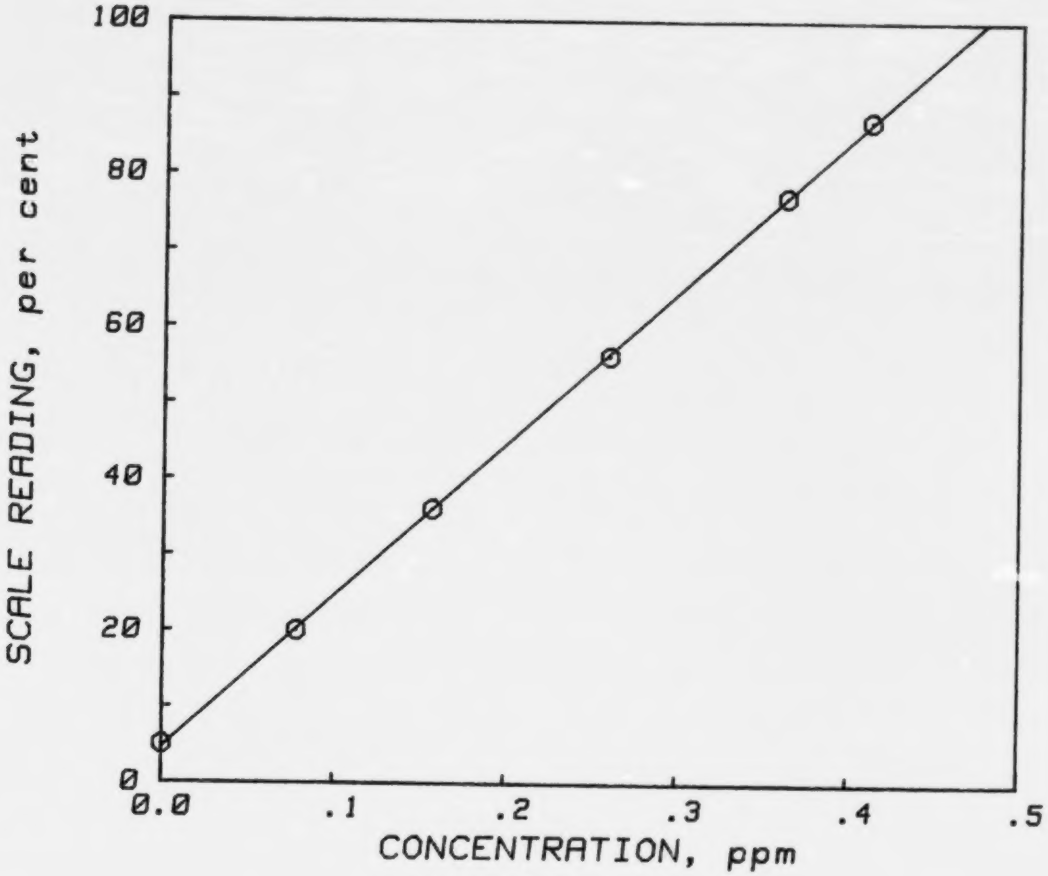
[b] Average, from manufacturer's application for equivalency determination.

[c] Average, from EPA Phase I postdesignation tests.

[d] Concentration significantly below the target value of 10 ppb allowed for this performance parameter since decreased test concentrations here represent a more severe test condition.

[e] Quantitative tests with naphthalene were not conducted; instead, the test analyzer was shown to have no measurable response to a concentration of naphthalene which produced at least a mid-scale response when the cutter was removed.

[f] Average of absolute values.



```
ANALYZER:    THERMO ELECTRON Y = MX + A        DATA:  __X__      __Y__
MODEL:       43
SERIAL No.:  329464                             1    0.000       5.000
POLLUTANT:   SO2               M =  199.142      2     .078      20.000
RANGE:        .5 ppm            95% C.I.= ± 2.275 3     .157      36.000
LOCATION:    DAMDF                              4     .260      56.100
DATE:        03/30/79          A =     4.698    5     .363      77.000
DATE CODE:    79.089            95% C.I.= ±  .587 6     .412      87.000
NAME:        PHASE II
                               r =    .99997
```

Figure 56. Typical calibration curve for the Thermo Electron 43.

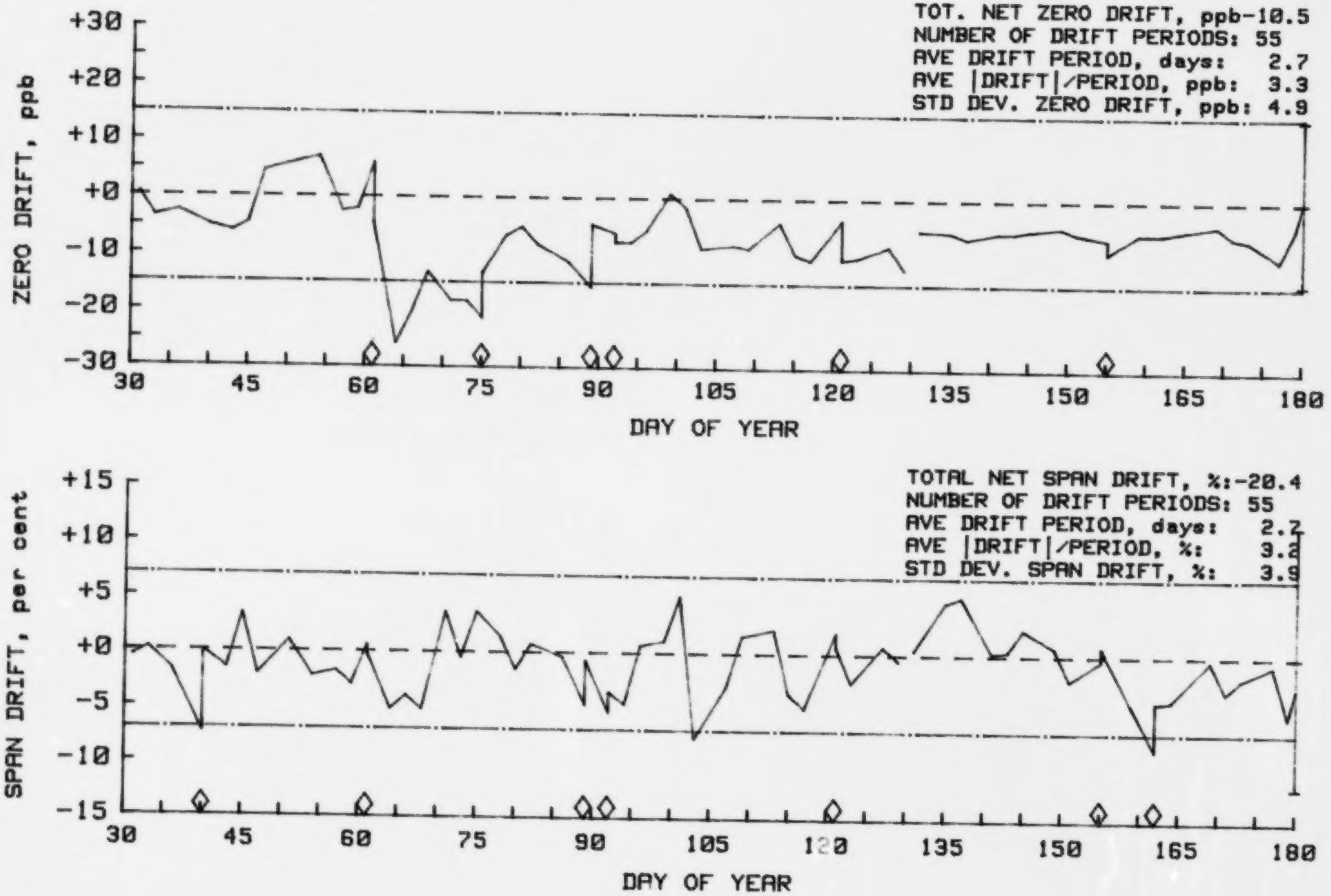


Figure 57. Zero and span drift in the Thermo Electron 43 SO_2 readings during the Phase II ambient monitoring test.

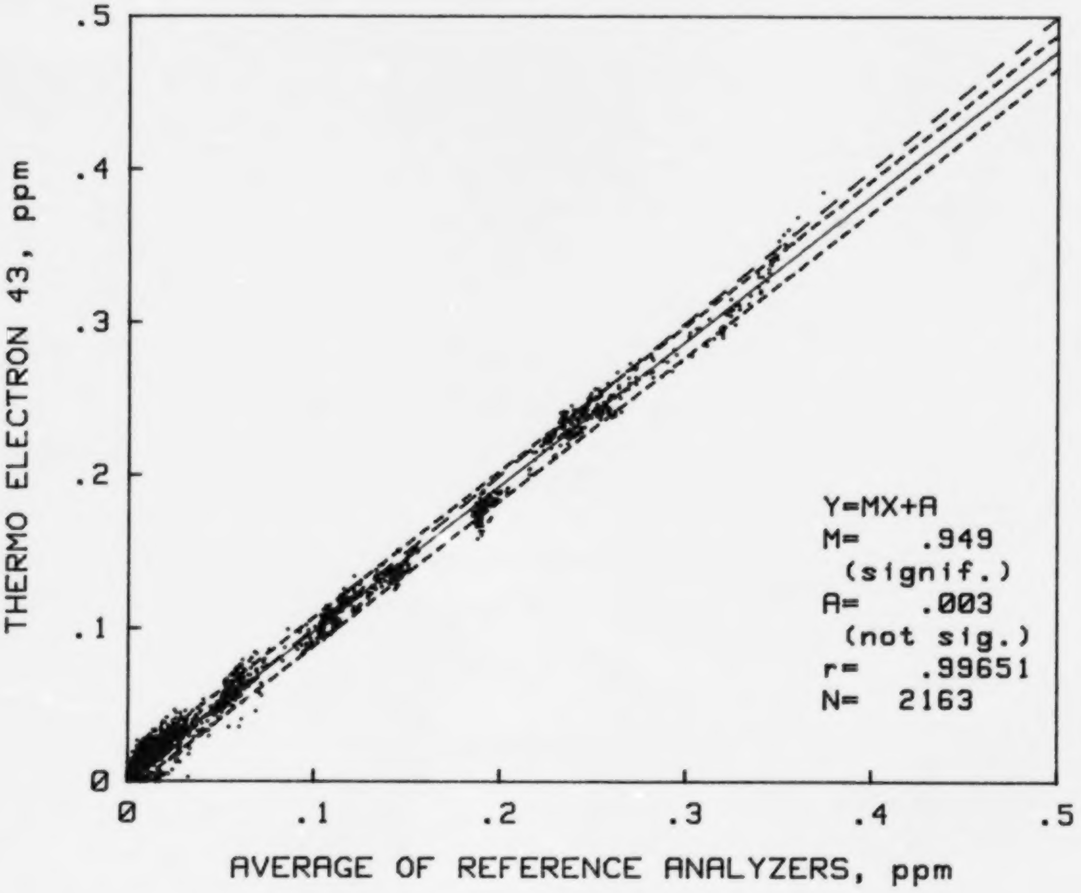
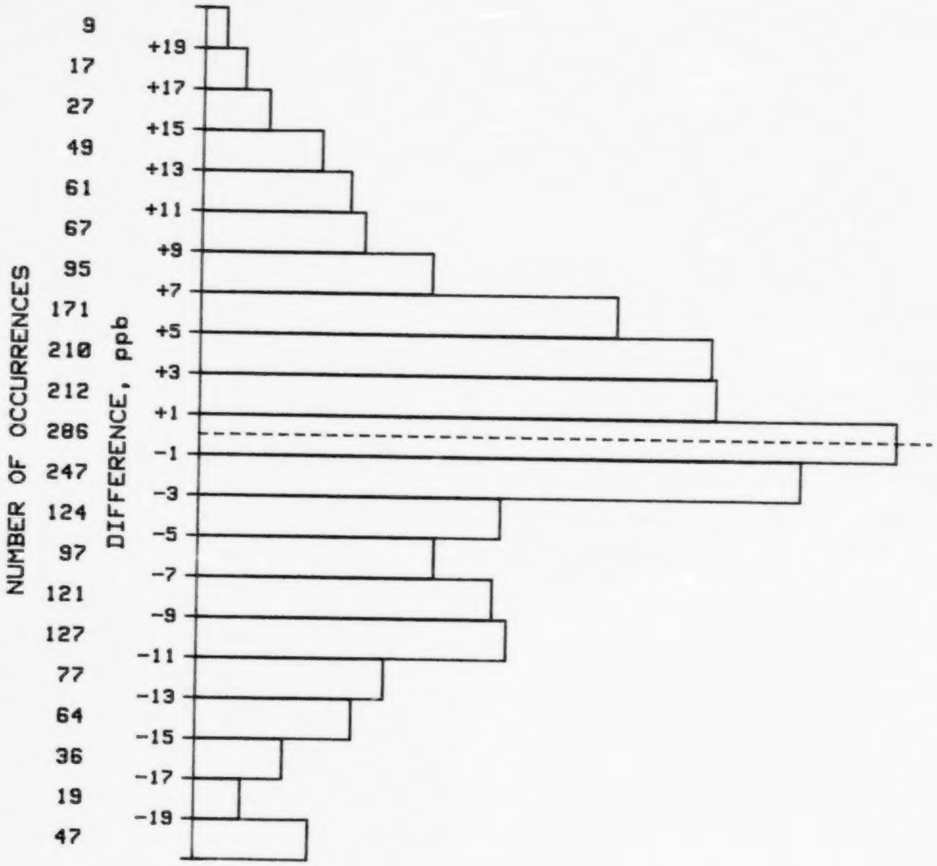
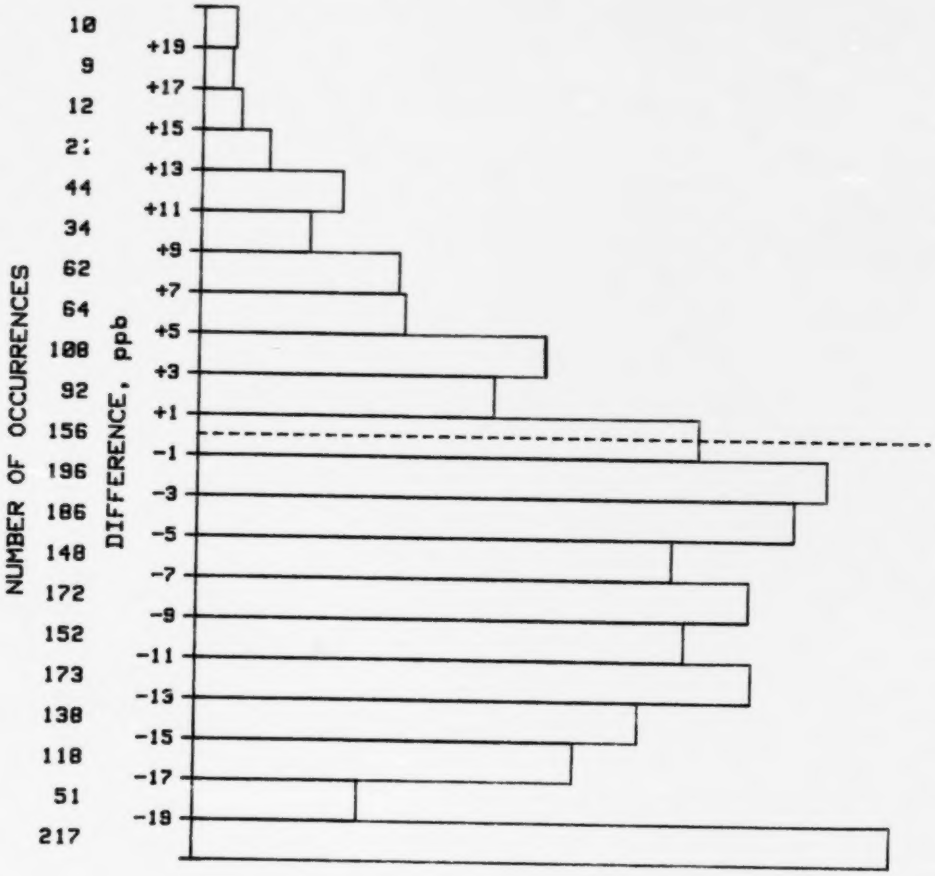


Figure 58. Relationship between the Thermo Electron 43 and the average of the other analyzers during the Phase II ambient monitoring test (before manufacturer's refurbishment--see General Comments).



```
TOTAL No. OF DATA PAIRS:                  2163
CORRELATION COEFFICIENT:                      .996505
MEAN DIFFERENCE, ppb:                       -.74
STD. DEVIATION OF DIFFERENCES, ppb:   8.2988
MAX. ABSOLUTE DIFFERENCE, ppb:          30
NO. ABSOLUTE DIFFERENCES >20:           49
```

Figure 59. Frequency distribution of differences in hourly SO_2 ambient air readings between the Thermo Electron 43 and the average of simultaneous readings from the other analyzers during the Phase II ambient monitoring test (before manufacturer's refurbishment--see General Comments). All readings corrected for zero and span drift.



```
TOTAL No. OF DATA PAIRS:                2163
CORRELATION COEFFICIENT:                     .994618
MEAN DIFFERENCE, ppb:                     -6.99
STD. DEVIATION OF DIFFERENCES, ppb:  11.4140
MAX. ABSOLUTE DIFFERENCE, ppb:           54
NO. ABSOLUTE DIFFERENCES >20:          211
```

Figure 60. Frequency distribution of differences in hourly SO_2 ambient air readings between the Thermo Electron 43 and the average of simultaneous readings from the other analyzers during the Phase II ambient monitoring test (before manufacturer's refurbishment--see General Comments). Thermo Electron 43 readings are <u>not corrected for zero and span drift</u>.

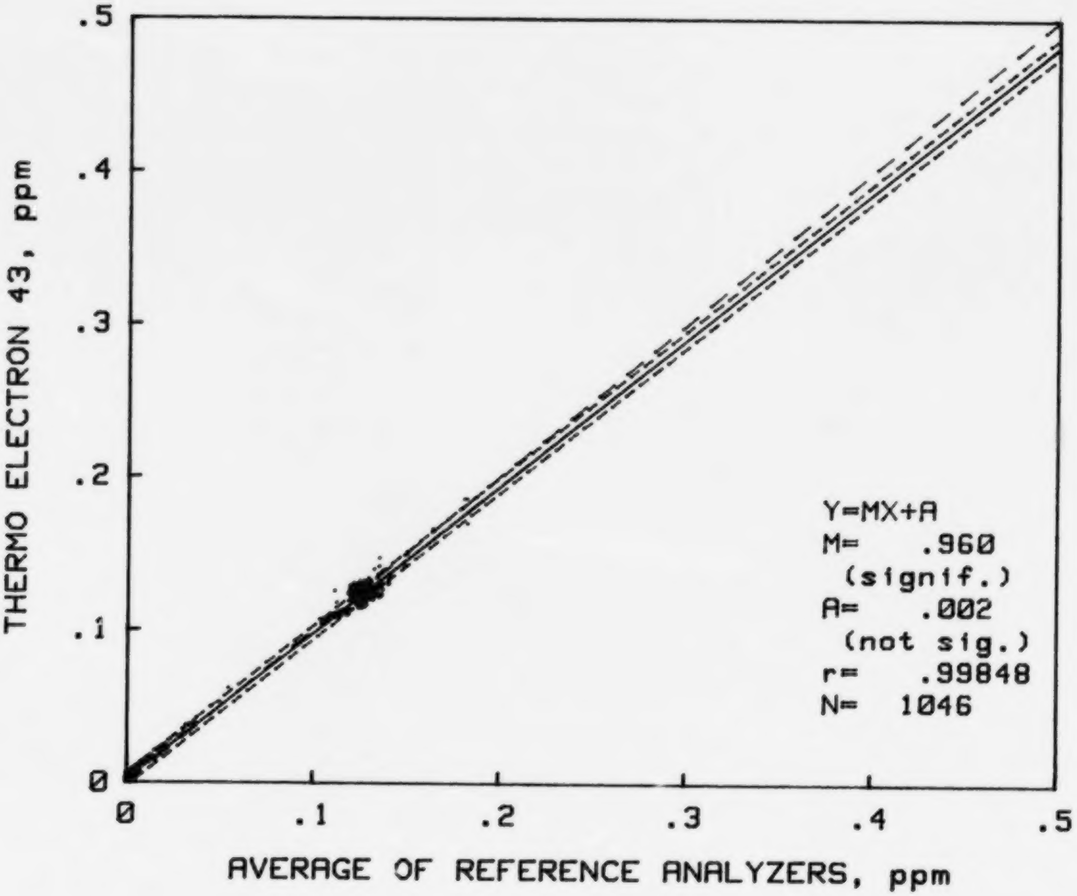
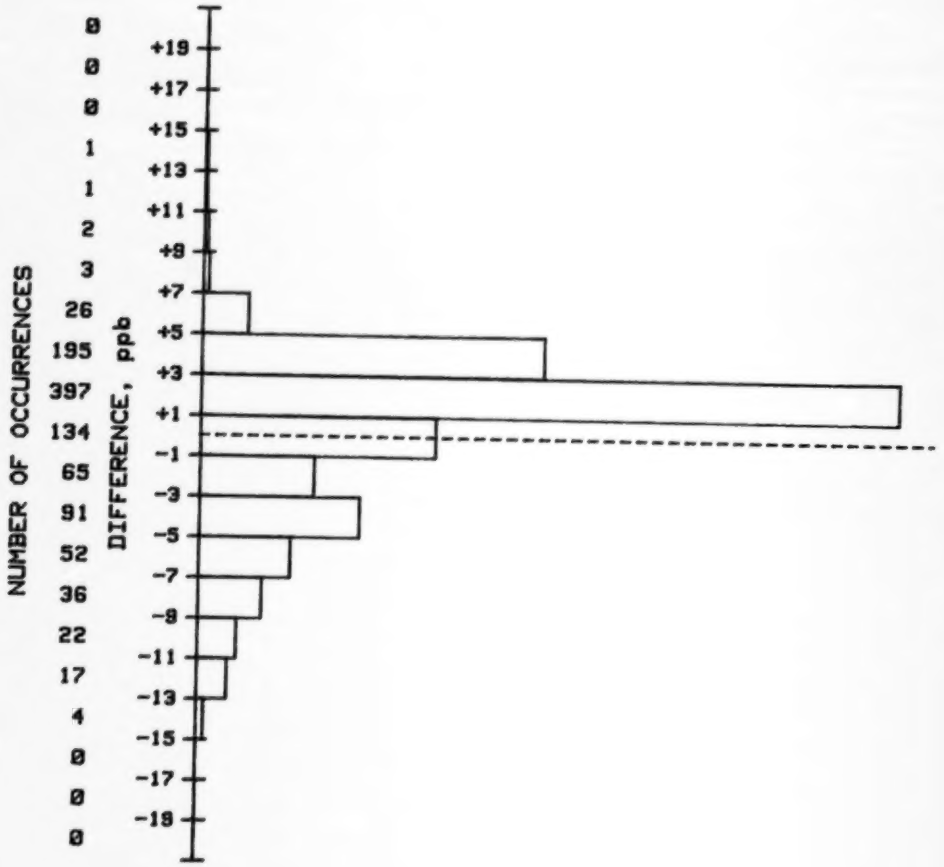
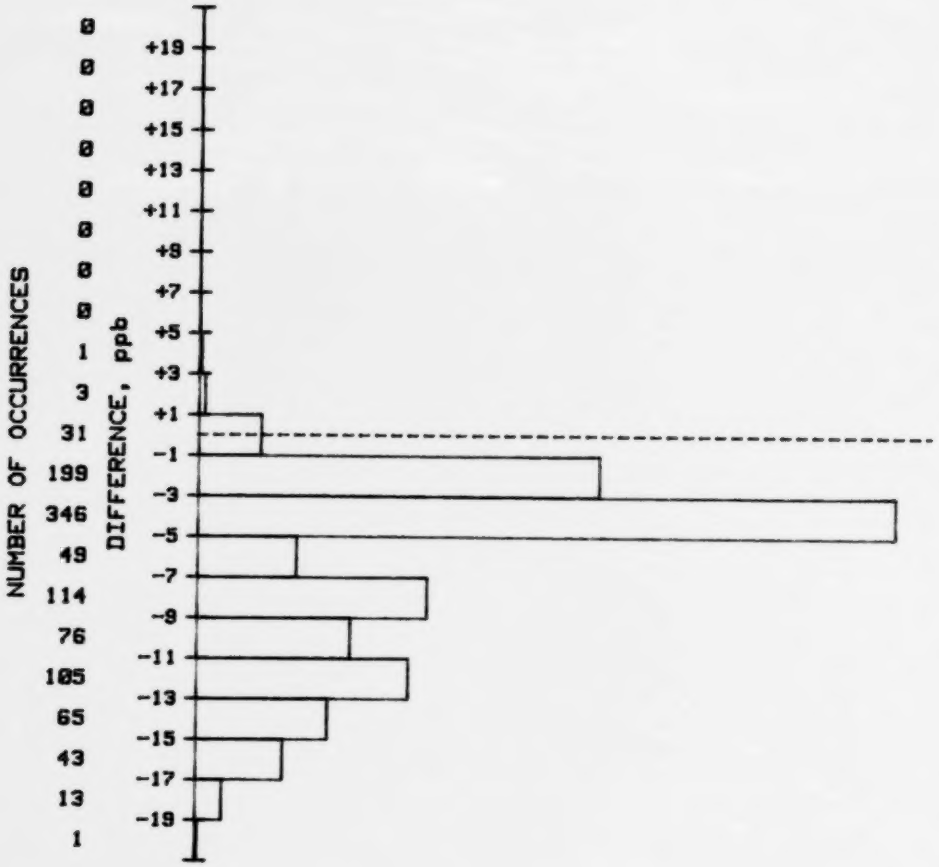


Figure 61. Relationship between the Thermo Electron 43 and the average of the other analyzers during the Phase II ambient monitoring test (after manufacturer's refurbishment--see General Comments).



TOTAL No. OF DATA PAIRS:	1046
CORRELATION COEFFICIENT:	.998475
MEAN DIFFERENCE, ppb:	+.20
STD. DEVIATION OF DIFFERENCES, ppb:	4.0650
MAX. ABSOLUTE DIFFERENCE, ppb:	14
NO. ABSOLUTE DIFFERENCES >20:	0

Figure 62. Frequency distribution of differences in hourly SO_2 ambient air readings between the Thermo Electron 43 and the average of simultaneous readings from the other analyzers during the Phase II ambient monitoring test (after manufacturer's refurbishment--see General Comments). All readings corrected for zero and span drift.



```
TOTAL No. OF DATA PAIRS:               1046
CORRELATION COEFFICIENT:                  .998607
MEAN DIFFERENCE, ppb:                   -6.53
STD. DEVIATION OF DIFFERENCES, ppb:      4.5567
MAX. ABSOLUTE DIFFERENCE, ppb:          20
NO. ABSOLUTE DIFFERENCES >20:            1
```

Figure 63. Frequency distribution of differences in hourly SO_2 ambient air readings between the Thermo Electron 43 and the average of simultaneous readings from the other analyzers during the Phase II ambient monitoring test (after manufacturer's refurbishment--see General Comments). Thermo Electron 43 readings are <u>not corrected for zero and span drift</u>.

Manufacturer's Recommended Maintenance

Operation	Frequency
Inspect sample filter.	Every 30 days
Inspect, clean, or replace sample capillary.	Every 6 mo
Inspect and clean fan filter.	Every 6 mo
Replace hydrocarbon cutter.	Every 18 mo

Malfunctions

Refurbishment of analyzer because of noise response on 5-9-79.

General Comments

Special hydrocarbon interferent tests were run during Phase I testing using the following compounds as potential interferents:

- 2,3-dimethylbutane
- 2-methylpentane
- 3-methylpentane
- 2,3-dimethylpentane
- 2,2,4-trimethylpentane
- 2,3,4-trimethylpentane
- 1-pentene
- 3-methylhexane
- heptane
- benzene
- 1,3,5-trimethylbenzene
- 1-ethyl-3-methylbenzene.

Of these compounds, only the three aromatic hydrocarbons (benzene, 1,3,5-trimethylbenzene, and 1-ethyl-3-methylbenzene) produced a response on the analyzer even without the hydrocarbon cutter. Of these three, benzene and 1,3,5-trimethylbenzene produced a response on the analyzer equipped with the cutter at concentrations greater than 2 ppm.

Initial evaluation of Phase II test data in April 1979 showed that the standard deviation of the differences between the Thermo Electron analyzer and the average of the other analyzers was larger than expected (see Figures 58 through 60). This deviation seemed to result from random variability in the instrument response. Because this instrument had been in service for 22 months before Phase II testing began, this apparent variability problem was attributed to aging of the instrument subassemblies. Thermo Electron service personnel were contacted, and they agreed that aging could be the cause. On May 9, 1979, the instrument was refurbished by factory personnel onsite at the EPA test facility. The refurbishment included replacement of the following:

- Fluorescence chamber
- PMT
- Flash lamp
- Zero and span solenoids
- Permeation dryer
- Hydrocarbon cutter
- Optics subassembly.

Before service, the mean difference and standard deviation of the ambient data were -0.7 ppb and 8.3 ppb, respectively. After service, the mean difference and standard deviation became +0.2 ppb and 4.1 ppb, respectively (see Figures 61 through 63).

During 215 days of Phase II testing, data were lost for 1 day because of malfunctions.

Phase II Testing Operator's Comments

Throughout the duration of the Phase II testing, this instrument showed a tendency to drift in the direction of a zero or span adjustment for approximately 24 h after adjustment. This drifting took place even though the instrument seemed to produce a stable strip chart trace about 10 min after the adjustment. Typically, the instrument would drift about 5 percent of scale beyond the adjustment point in 24 h.

An unusual characteristic of this analyzer is that the span pot must be reduced to increase the span response.

This analyzer achieved equilibrium on span gases in less than 5 min.

The instruction manual for this analyzer is confusing in certain places where it describes, in detail, how to perform a certain operation (e.g., how to clean the fluorescence chamber) but makes no mention of when or under what circumstances to perform the operation.

APPENDIX A

MEASUREMENT PRINCIPLES EMPLOYED BY DESIGNATED SO_2 ANALYZERS

The SO_2 instruments currently designated operate according to one of the following measurement principles:

- Flame photometric detection
- Fluorescence detection
- Second derivative spectroscopic detection
- Coulometric detection
- Conductometric detection.

Brief descriptions of each of these measurement principles are presented below to enhance understanding of the similarities and differences among various designated analyzers.

FLAME PHOTOMETRIC DETECTION

This principle is based on the photometric detection of the chemiluminescence (light produced by a chemical reaction) from sulfur atoms in a hydrogen-rich flame. The sample gas (containing the sulfur compounds) is mixed with hydrogen and burned, producing (among other products) a molecular sulfur species, S_2. This species is raised to an elevated electronic energy state (S_2^*) by interaction with hydrogen ($H\cdot$) or hydroxyl ($\cdot OH$) radicals also produced in the burning process. As the activated species decays to its energy ground state, it releases energy in the form of light. This light covers a broad range of wavelengths with a maximum intensity at 394 nm. The light intensity is essentially proportional to the square of the sulfur concentration in the flame and thus is related to the volumetric concentration of sulfur-containing molecules in the sample gas. The light energy is sensed by a photomultiplier tube (PMT), which produces an output current proportional to the light energy. This current, converted to a voltage and conditioned as necessary by the electronic circuits, becomes the analyzer's output reading or signal. Characteristically, flame photometric detectors (FPD) produce an output signal that is exponentially related to the sulfur concentration. However, all currently designated analyzers have electronics capable of linearizing this output. Most analyzers include this linearizer as standard equipment, but on at least one model it must be procured as an option.

Several important points must be considered concerning the use of flame photometry for ambient SO_2 analyses. First, flame photometric detection is sensitive to all sulfur-containing molecules. For this principle to be specific for SO_2, the sample stream must be scrubbed by appropriate means upstream of the detector to remove ambient sulfur species other than SO_2. Scrubbing is usually accomplished by either an ambient-temperature chemical scrubber or a heated silver scrubber. These scrubbers remove ambient hydrogen sulfide but do not remove other reduced sulfur species such as methyl mercaptan. However, this is a minor problem because the air at most monitoring sites rarely contains significant quantities of reduced sulfur compounds other than H_2S.

One prevalent problem with heated silver scrubbers is that the scrubber can generate both positive and negative interferences in the presence of ambient ozone. The positive interferences may occur according to the following mechanism. Ambient hydrogen sulfide is removed from the sample stream by reaction with the silver, forming silver sulfide according to the equation:

$$H_2S + 2Ag \rightarrow Ag_2S + H_2 \ .$$

In the presence of--or on subsequent exposure to--ozone, however, the silver sulfide probably continues to react where:

$$3Ag_2S + 2O_3 \rightarrow 6Ag + 3SO_2$$

or

$$Ag_2S + O_3 \rightarrow Ag_2O + SO_2 \ .$$

Either way, the H_2S entering the scrubber is eventually converted to SO_2 and detected as a positive interference.

The negative interference in the presence of O_3 probably follows a more obscure mechanism. The result, nevertheless, is the removal of SO_2 from the sample stream, perhaps by conversion (in the presence of the silver) to the sulfate ion occurring in the form of sulfuric acid. Both the positive and negative interferences in the presence of ozone can be minimized by decomposing the ozone in the sample stream prior to its reaching the silver. This process is most often accomplished thermally, but one presently designated method uses ethylene to assist in decomposition.

A second point to consider when FPD is used is that the technique is subject to quenching of the chemiluminescence by common ambient gases such as oxygen and carbon dioxide. Therefore, it is important to maintain reasonably constant concentrations of these gases between the calibration matrix and the sample matrix. Difference in oxygen concentrations between the two matrices can become significant if a low-level SO_2-in-nitrogen cylinder gas is diluted to prepare a calibration standard. In such a case, the nitrogen in the pollutant flow stream may "dilute" the oxygen in the dilution air stream, significantly decreasing oxygen concentration. This situation can be avoided by keeping the concentration of SO_2 in the cylinder gas high enough that the nitrogen contributed by the pollutant flow stream is insignificant with respect to the total flow volume.

Differences in CO_2 concentrations between calibration and sample matrices become significant when sources of zero air that contain no CO_2 (ambient CO_2 concentration is at least 320 ppm) are used for calibration. This often occurs because many systems used for preparing zero air remove CO_2. Also, most cylinders of compressed synthetic air sold as zero-grade air contain no CO_2. This problem can be avoided by using zero air systems that specifically pass CO_2 and by supplying their intakes with outdoor ambient air. Zero-grade compressed air, which contains approximately 320 ppm CO_2, may also be ordered from commercial gas suppliers.

One further point to remember when FPD is employed for SO_2 analyses is that FPD analyzers require a source of pure, dry hydrogen. This requirement involves extra effort for the handling and maintenance of support gas cylinders or hydrogen generators. The use and handling of hydrogen also involves additional safety precautions because this gas is flammable or explosive when mixed with air.

FLUORESCENCE DETECTION

This principle is based on detection of the characteristic fluorescence released by the sulfur dioxide molecule when it is irradiated by ultraviolet light. This fluorescent light is also in the ultraviolet region of the spectrum, but at a different wavelength than the incident radiation. The fluorescent wavelengths usually monitored are between 190 and 230 nm. In this region of the spectrum, there is relatively little quenching of the fluorescence by other molecules occurring in ambient air. As in flame photometry, the light is detected by a PMT that, through the use of electronics, produces a voltage proportional to the light intensity and SO_2 concentration.

The fluorescent light reaching the PMT is usually modulated to facilitate the high degree of amplification necessary. Some analyzers mechanically "chop" the incident irradiation before it enters the reaction chamber. This process is accomplished by a fan-blade-like chopper rotating at a constant speed, which alternately blocks and passes the light to the chamber. Other instruments electronically pulse the incident light source at a constant rate.

Potential interferences to the fluorescence technique include any species that either quenches or exhibits fluorescence. Both water vapor and oxygen strongly quench the fluorescence of SO_2 at some wavelengths. Where water vapor presents a problem, it can be removed by a dryer within the instrument. In most analyzers, the water interference is minimized by careful selection of the incident radiation wavelength. The effect of oxygen quenching can be minimized by maintaining identical oxygen concentrations in the calibration and sample matrices, as discussed with respect to flame photometry.

Aromatic hydrocarbons such as naphthalene exhibit strong fluorescence in the same spectral regions as SO_2 and are major interferents. These aromatics must be removed from the sample gas stream by an appropriate scrubber upstream of the reaction chamber. The scrubbers may operate at ambient or elevated temperature. Certain elevated-temperature scrubbers, however, have the potential for converting ambient hydrogen sulfide (which normally does not interfere with the fluorescence technique) into SO_2. In these cases, the hydrocarbon scrubber must be preceded by a scrubber for H_2S.

SECOND DERIVATIVE SPECTROSCOPIC DETECTION

Many gases absorb light at various wavelengths. In particular, gases often absorb light in narrow, specific intervals of wavelength. This means that a gas may absorb strongly at a certain wavelength but may exhibit less absorption just a few wavenumbers to either side of that wavelength. These narrow intervals, called absorption bands, are characteristic of a specific gas, and the sharpness of a specific absorption peak is used as the basis of second derivative spectroscopy.

In conventional spectroscopy, light of a fixed wavelength is passed through a gas and detected by a PMT. The reduction in light intensity because of absorption at that fixed wavelength is exponentially related to the concentration of the gas according to Beer's Law. In the case of an ambient air sample, other gases may be present that also absorb at the fixed wavelength and therefore interfere with the measurement. However, if a wavelength can be found at which the gas of interest has a very sharp, narrow absorption peak, while other gases that might be present exhibit a broad, widely distributed absorption, second derivative spectroscopy can be used to measure the gas of interest with minimal interference. This is possible because second derivative spectroscopy measures the "sharpness" (i.e., the second derivative) rather than the magnitude of the peak.

The absorption peak sharpness is measured by selecting a wavelength centered in a narrow absorption band of the gas of interest--SO_2--in the near ultraviolet spectral region. The specific absorption band selected must have a strong absorption peak and be free of overlapping sharp absorption peaks from other gases likely to be present in the sample. The second derivative spectrometer has a way to vary the wavelength periodically slightly above and slightly below the center wavelength so higher and lower wavelengths fall on the sides of the absorption peak, well below the maximum. The instrument compares the absorption at the center wavelength to the absorption at the two side wavelengths, which is a measure of the curvature of the absorption peak. Because the other absorbing gases have broadband absorption, their contribution to the absorption is almost identical at the three wavelengths; hence, they have little effect on the curvature measurement. The sharpness of the absorption peak is directly proportional to the height of the peak, which is, in turn, related to the gas concentration of the SO_2 according to Beer's Law. Hence, the concentration measurement is highly specific for SO_2 without the use of chemical scrubbers or other sample conditioning components. Suitable electronic circuits in the analyzer control the wavelength variation, make the absorption measurements, compute the curvature, and provide an output signal representative of the concentration measurement.

A point to remember when using this technique is that the incident light must pass through a "long" sample path to achieve sufficient sensitivity. A typical pathlength of 12 meters is obtained with a "folded path" cell, where the light is bounced back and forth several times through a shorter cell. This necessitates the use of a precise, ultraviolet optical system, which has significant optical losses and is often difficult to align and keep aligned. In addition, optical systems exposed to ambient air may need frequent cleaning. Finally, the optical system necessary to obtain and vary the narrow, accurate wavelength band is often delicate and difficult to adjust.

COULOMETRIC TITRATION DETECTION

The principle of continuous coulometric titration depends on maintaining an equilibrium between ionic species in an electrolyte so the redox (reduction-oxidation) potential between two electrodes in the electrolyte remains constant. For SO_2 monitoring, the electrolyte is usually dilute sulfuric acid (H_2SO_4) and the species in equilibrium are usually free bromine (Br_2) and the bromide ion (Br^-).

In an acid medium, free bromine and the bromide ion interact to establish an equilibrium according to the equation:

$$2Br^- \rightleftarrows Br_2 + 2e^- \ .$$

As long as the temperature of this medium remains constant, the Nernst equation predicts that the equilibrium potential produced by this interaction will remain constant. When SO_2 is introduced into this equilibrium by bubbling the sample gas stream through the H_2SO_4 solution, free bromine is reduced to the bromide ion according to the equation:

$$SO_2 + Br_2 + 2H_2O \rightarrow H_2SO_4 + 2Br^- + 2H^+ \ .$$

This reaction upsets the previously established equilibrium, resulting in changed potential across the electrodes.

When this change in potential is sensed by the analyzer's electronics, a current is applied to a second set of electrodes in the medium. This current causes the generation of free bromine from the bromide ion and tends to reestablish the original equilibrium, which reestablishes the original equilibrium potential. The current necessary to reestablish the equilibrium is linearly proportional to the mass of bromine consumed, which is, in turn, linearly proportional to the mass of SO_2 entering the reaction. This current is converted electronically into a suitable voltage that becomes the analyzer's concentration measurement output signal.

Any species in the sample gas stream that has the ability to reduce bromine chemically (or, conversely, be oxidized by bromine) represents an interference to the measurement principle. In fact, any species that can upset the bromine/bromide equilibrium, such as through consumption or augmentation of the bromide ion, is a potential interferent. Careful, selective scrubbing of the sample gas stream is necessary to avoid such interference.

Analyzers using the coulometric technique require periodic replenishment or replacement of the electrolyte. The entire measuring chamber, and particularly the electrodes, must be kept scrupulously clean. Stable flow control is essential for mass-sensitive analyzers. Flow control devices (e.g., orifices and valves) may require substantial maintenance when used in wet-chemical systems where they are subject to continuous contamination and degradation by corrosive chemicals used in the system.

CONDUCTIMETRIC DETECTION

This principle is based on increased electrical conductivity of an oxidizing, acid-measuring solution when it absorbs SO_2. The only currently designated instrument that uses this principle (the ASARCO 500) employs a dilute solution of sulfuric acid containing a small amount of hydrogen peroxide as the oxidizing agent.

As ambient air (containing SO_2) is bubbled through the measuring solution, the SO_2 is oxidized to the sulfate ion by the action of the hydrogen peroxide according to the equation:

$$SO_2 + H_2O_2 \rightarrow SO_4^{=} + 2H^{+} .$$

The formation of additional sulfate ions increases the conductivity of the solution. Two platinum electrodes, placed in the solution and connected to a balanced bridge circuit in a recorder, record this increased conductivity. Because the conductivity of any solution is temperature dependent, provisions are made for temperature compensation through the use of a temperature compensator immersed in the solution.

Any gas present in the atmosphere that will ionize in an aqueous medium (e.g., dilute sulfuric acid) will increase the conductivity of the measuring solution used in this principle. Such an increase represents a positive interference in the measurement of SO_2. Nitrogen dioxide and carbon dioxide are examples of these gases, which are routinely present in ambient air. Ammonia and hydrogen chloride will also ionize in solution but are not so prevalent in the atmosphere. Also, any species present in the atmosphere that can decrease solution conductivity (perhaps by chemically complexing previously ionized species) represents a negative interference. To prevent such interferences, the sample gas must be chemically scrubbed of all such species before it is introduced into the measuring solution.

Although a conductometric analyzer could be designed with a dynamic, continuously flowing measurement cell, the ASARCO uses a batch operation with a fixed volume of static electrolyte. Because the conductivity of the static electrolyte increases in proportion to the SO_2 concentration and remains constant when the SO_2 concentration is zero, the result is that the measured conductivity represents the accumulated (integrated) SO_2 concentration. Periodically, the cell is (automatically) emptied and refilled with fresh electrolyte to start a new cycle. The instantaneous SO_2 concentration can be derived by differentiating (finding the slope with respect to time) of the conductivity measurement. However, because hourly average SO_2 concentrations are normally needed, the integrated SO_2 reading represented by the maximum conductivity reading for each cycle (obtained just prior to refilling) is conveniently used to obtain the hourly average (two cycles per hour). A special dynamic calibration procedure (described in the analyzer's operation manual) is used to accommodate the cyclic, batch operation.